NOTICE
TO INTENDING AUTHORS

1. Manuscripts for publication should be sent to the Assistant Editor, Indian Journal of Physics, Jadavpur, Calcutta-32.

2. The manuscripts submitted must be type-written with double space on thick foolscap paper with sufficient margin on the left and at the top. The original copy, and not the carbon copy, should be submitted. Each paper must contain an Abstract at the beginning.

3. All References should be given in the text by quoting the surname of the author, followed by year of publication, *e.g.*, (Mazumder, 1959). The full Reference should be given in a list at the end, arranged alphabatically, as follows; Mazumder, M. 1959, *Ind. J. Phys.*, **33**, 346.

4. Line diagrams should be drawn on white Bristol board or tracing paper with black Indian ink, and letters and numbers inside the diagrams should be written neatly in capital type with Indian ink. The size of the diagrams submitted and the lettering inside should be large enough so that it is legible after reduction to one-third the original size. A simple style of lettering such as gothic, with its uniform line width and no serifs should be used, *e.g.*,

A·B·E·F·G·M·P·T·W·

5. Photographs submitted for publication should be printed on glossy paper with somewhat more contrast than that desired in the reproduction.

6. Captions to all figures should be typed in a separate sheet and attached at the end of the paper.

7. The mathematical expressions should be written carefully by hand. Care should be taken to distinguish between capital and small letters and superscripts and subscripts. Repetition of a complex expression should be avoided by representing it by a symbol. Greek letters and unusual symbols should be identified in the margin. Fractional exponents should be used instead of root signs.

EMISSION BAND SPECTRUM OF SeO$_2$ MOLECULE

P. B. V. HARANATH,* AND V. SIVARAMAMURTY

PHYSICS DEPARTMENT, ANDHRA UNIVERSITY, WALTAIR

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Plate XIV

ABSTRACT. The emission spectrum of pure SeO$_2$ vapour as excited in a high frequency discharge from an oscillator and in an uncondensed discharge from a transformer, is found to reveal a number of characteristic bands in the region λ 4700 to λ 2750. These bands are diffuse and are attributed to the emitter, the triatomic SeO$_2$ molecule. About 100 bands in the region λ4700 to λ3200 are analysed as belonging to two new systems of SeO$_2$ molecule arising out of transitions from the deformation vibrational levels of the upper states to symmetric vibrational levels of the lower states. The following are the vibrational constants of the two systems.

	$\nu_{0,0,0}$	Sym. vib. frequency of lower state	Def. vib. frequency of upper state
System—I.	32145 cm^{-1}	910.5 cm^{-1}	182 cm^{-1}
System—II.	32052 cm^{-1}	911.5 cm^{-1}	182 cm^{-1}

Bands below λ3200 down to λ2750 are found to belong to a part of the B → X system of SeO$_2$ molecule observed previously in absorption.

INTRODUCTION

In our recent investigation on the spectra of the dioxides of selenium and tellurium, it has been found that the emission of pure SeO$_2$ vapour excited in electrical discharges revealed a characteristic band spectrum consisting of a number of new bands in the visible and near ultraviolet region. The origin and nature of these new bands have been discussed in this paper.

EXPERIMENTAL

Selenium dioxide employed in the present investigation is a white powder which sublimes at 315°C. The substance was perfectly dehydrated before it was introduced into the discharge tube. Spectra were excited by an oscillator of approximately 50 Watt output power at 10 m.c.s. frequency and in an uncondensed discharge from a 10 KV transformer. The oscillator discharge tube was an ordinary pyrex glass tube of 30 cm. in length and 20 mm in diameter. One end of the tube was drawn into an adaptor and was connected to a system of high vacuum pumps. The other flat end was closed by a quartz window. The electrodes drawn directly across the tank circuit of the oscillator, were wrapped

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*National Research Fellow.

round the discharge tube. A flowing vapour of the substance was maintained inside the tube by continuous evacuation and by occasional heating with Bunsen flame,

In the case of transformer discharge experiments, a similar discharge tube was employed but provided with two side limbs at 10 cm apart fused with tungsten electrodes to which the high tension of 10KV was applied. In both these discharges the colour of the emission free from usual impurities is deep blue.

Spectra were photographed on Hilger Medium Quartz, Fuess, Hilger's Quartz Littrow and Glass Littrow spectrographs and were recorded on Ilford Special Rapid plates. The times of exposures were of 5 to 10 minutes duration on the low dispersion instruments and of 20 to 30 minutes duration on the high dispersion instruments.

RESULTS

The emission of SeO_2 vapour excited in different electrical discharges revealed a characteristic spectrum of a number of bands in the region $\lambda 4700-\lambda 2700$. Plate XIV, Fig. 1(a) and (b) are the reproductions of the spectra photographed on the medium quartz instrument. The band heads in the region $\lambda 4700-\lambda 3200$ (strip-a) appear diffuse and those below $\lambda 3200$ down to $\lambda 2700$ (strib-b) are sharp and red degraded. Each of these diffuse bands when photographed on high dispersion Littrow spectrographs, was resolved into a number of component heads of different intensities which might correspond probably to the isotopic effect of selenium in the SeO_2 molecule. About 100 band heads in the region $\lambda 4700-\lambda 3200$ were measured on a number of high dispersion plates and the accuracy of the band head data was found to be within the limits of 2 to 3 cm^{-1}.

The wavelength data of these new bands were compared with the band head data of the well known spectra of the diatomic SeO and Se_2 molecules excited under similar conditions. They totally disagree and the spectra of the three molecules appear entirely different from each other. On the other hand, the new bands do not appear to possess the characteristic rotational structure, even when photographed on the high dispersion instruments, which should be the case if they belong to the diatomic SeO molecule. On the basis of this experimental evidence, the 100 bands in the region $\lambda 4700-\lambda 3200$ obtained in the present investigation, could tentatively be assigned to the triatomic emitter SeO_2 molecule. The sharp red degraded bands in the region below $\lambda 3200$ to $\lambda 2700$ were found to belong to a part of the priviously known *B-X* system of SeO_2 observed in absorption by Duchesne and Rosen (1941).

ANALYSIS OF THE BANDS

Already three systems namely, A, B and C, are observed (Choong Shin Piaw. 1938 ; Duchesne and Rosen, 1947) in absorption of SeO_2 vapour in which B and C

TABLE I

Vibrational analysis of system I

$v_2'' \backslash v_1'$	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0.	32145	31234	30332	29426	28535	27645	26762	25883	25010	24144	23289	—	21599	—
1.	32326	31416	30511	29614	28713	27833	26946	26068	25195	24323	23470	22617	—	—
2.	—	—	30695	29798	28889	28007	27125	26252	25370	24501	23651	22795	22795	—
3.	—	—	—	29975	29068	28184	27301	26410	25547	24681	23822	—	—	—
4.	—	—	—	30148	29248	28366	27471	26592	25728	24860	23992	—	—	—
$\Delta G(v_2'')$	910.5	903.5	900	900	884	884	880	871	868	857	845.5			

TABLE II

Vibrational analysis of system II

$v_2'' \backslash v_1'$	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0.	32052	31143	30226	29339	28446	27552	26668	25790	24919	24054	23200	22356	21520	—
1.	32234	—	30423	29523	28626	27732	26848	25973	25097	24238	23379	22537	21703	—
2.	—	31499	30601	29699	28804	27913	27032	26152	25277	24412	23558	22710	21882	21053
3.	—	—	30779	—	28982	28089	27213	26327	25456	24589	23736	22888	—	—
4.	—	—	—	—	29101	28270	—	26503	25633	24754	23910	—	—	—
$\Delta G(v_2'')$	909	902.5	900	895	893	881	881	880	873	867	853	833	829	

occurring in the regions $\lambda3400-\lambda2200$ and $\lambda4500-\lambda3400$ respectively, are more extensive. There are possibilities that the present emission bands in the region $\lambda4700-\lambda3200$, might either belong to system C or form an extension of system B. No agreement was found between the wave-length data of these emission bands and the absorption bands of C-X system occurring in this region. Attempts made to extend the analysis of B-X system to include the present emission bands yielded no satisfactory analysis. The emission bands above $\lambda3200$ appear diffuse whereas the bands below $\lambda3400$ belonging to the B-X system are sharp and red degraded. As such, the series of emission bands in the region $\lambda4700$-$\lambda3200$ cannot be attributed to either of the two systems B and C and are to be considered as forming one or more new systems of SeO_2 molecule.

The whole series of new bands in the region $\lambda4700$-$\lambda3200$ are analysed as belonging to two new overlapping systems to each of which every alternate band belongs. These two systems are designated here as Systems I and II and their vibrational analyses are presented in Tables I and II.

In both the systems, several characteristic long lower state progressions are developed. Some of these prominent progressions are marked in Plate XIV, Fig. 1(a) & (b). An average difference of 910 cm^{-1} is observed between the successive bands near origin of the system in each progression of the two systems. This frequency of 910 cm^{-1} can be identified with or can be considered as a similar one to the previously known symmetric vibrational frequency $\omega''_2 = $ 910 cm^{-1} for the ground state of SeO_2 molecule derived from the absorption work of C-X system by Duchesne and Rosen (1947)

For each system, only four upper state progressions are formed with a characteristic difference of about 180 cm^{-1} between the successive bands. The low value of this frequency in each system suggests that this has to be identified as the deformation vibrational frequency of the corresponding excited states of SeO_2 molecule. Thus, the transitions observed in the two systems are from the vibrational levels of the upper states with deformation frequency $\omega'_1 = 182$ cm^{-1} to the vibrational levels of lower states with symmetric frequency $\omega''_2 = 910$ cm^{-1}.

The vibrational constants for the two emission systems as obtained from the analysis are as follows.

	$\nu_{0,0,0}$ cm^{-1}	Symmetric vib. frequency of the lower state ω''_2	$\chi''_2\omega''_2$	Def. vib. frequency of the upper state. ω'_1
System I	32145	910.5 cm^{-1}	3.0 cm^{-1}	182 cm^{-1}
System II	32052	911.5 cm^{-1}	2.5 cm^{-1}	182 cm^{-1}

Since, the corresponding average $\Delta G(v''_2)$ values of the lower state progressions are almost equal in the two systems, they might be considered of having a common

PLATE XIV
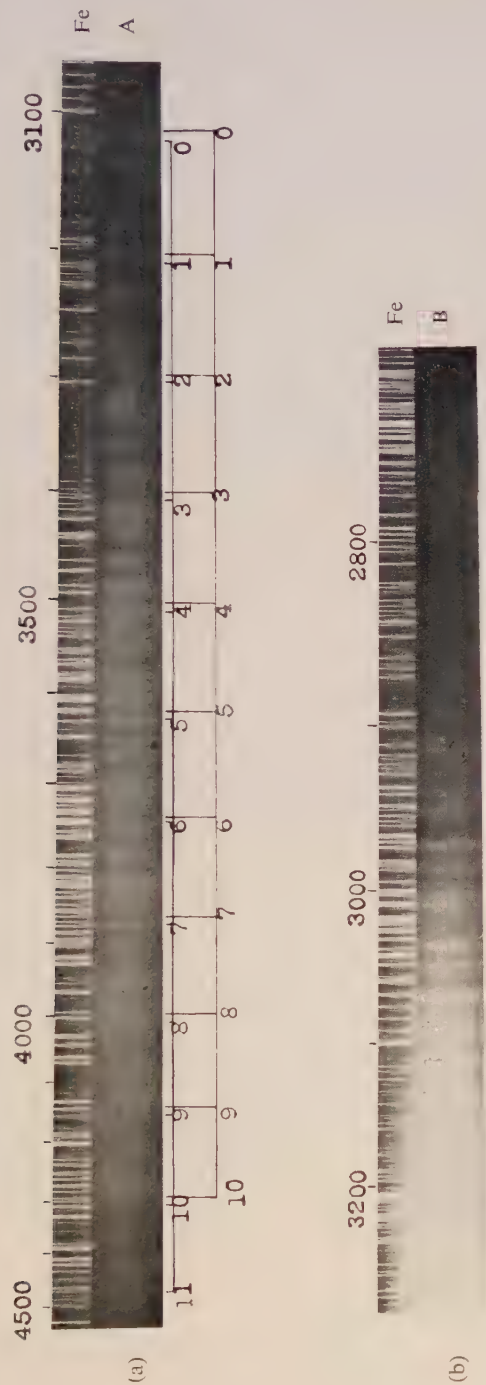
Fig. 1 (a) Emission spectrum of SeO2 Vapour (λ 4500 − λ 3200).
    (b) Emission spectrum of SeO2 Vapour (λ 3200 − λ 2700).

lower state. However, it is difficult to conclude whether this common lower state is the same as the normal state of SeO_2 molecule, since these bands are not observed in absorption.

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THE SHAPE OF THE TARGET MOLECULE AND THE DIFFUSION DISTANCE OF RADICALS FORMED BY IONIZING RADIATION

S. B. BHATTACHARJEE and N. N. DAS GUPTA

Biophysics Division,

Saha Institute of Nuclear Physics,

Calcutta-9, India.

ABSTRACT. The increased sensitivity of any micro-organism, when irradiated in wet condition, is explained by the radical formation in the film of water surrounding the vital molecules and the diffusion of these radicals to the vital molecules causing their inactivation. This diffusion distance can be obtained from a measurement of the doses of radiation for inactivation in the dry and wet conditions. This distance is a function of the shape of the vital molecule, the number of effective radicals per primary ionization and the ratio of dry to wet irradiation doses. In this paper is reported a simple method for estimation of this diffusion distance for an ellipsoidal target of any axial ratio for any measured value of dry and wet irradiation doses.

INTRODUCTION

Biological material is more sensitive to radiation in the wet than in the dry state of irradiation. This additional inactivation of biological samples, when irradiated in hydrated condition, is due to the formation of radicals in the water surrounding the vital molecules, some of which subsequently diffuse to these and inactivate them (Zirkle and Tobias, 1953; Hutchinson, 1957; Hutchinson and Ross 1959; Hutchinson and Norcross, 1960). The diffusion distance in the different cases has been estimated on the assumption of a spherical target. In a recent paper Hutchinson and Arena (1960) have calculated the diffusion distance in the case of irradiation of DNA *in vivo*. They assumed the model of a right cylinder.

In the present report, a simple theory has been developed for estimation of the diffusion distance for the general case of ellipsoidal target molecule. This method enables one to determine the diffusion distance for any measured values of dry and wet irradiation doses, for any axial ratio and for different probabilities of inactivation by radical formation.

This theory has been used to calculate the diffusion distance from the experimental data on dry and wet inactivation of different enzymes as presented by previous workers.

ANALYSIS OF INDIRECT EFFECT

If the inactivation is due to a single-hit type of process the survival ratio $S = N/N_0$ after dose of D rads is given by

$$S = \exp\,(-I\sigma V) \qquad \qquad \ldots \ (1)$$

where I is the number of primary ions per cc of unit density material produced by the dose D rads and V is the volume of a target molecule responsible for inactivation. Assuming that 1 rad of energy absorption releases $5.68 \times 10^{11}\sigma$ primary ions per cc of the target material of density σ, the total target volume V is given by

$$V = \frac{1}{D_d \times 5.7 \times 10^{11}\sigma} \ \ \text{cc} = \frac{1.76 \times 10^{12} \ \text{Å}^3}{D_d\sigma} \qquad \ldots \ (2)$$

where D_d is the dose of radiation giving 37 per cent survival in the dry condition.

If the target molecule be assumed as an ellipsoid of revolution with the semi--axes a and b, the axis of revolution being the b axis, the volume V is given by

$$V = \frac{4\pi}{3}\,ab^2 = 4.18pb^3 \ \text{Å}^3 \qquad \ldots \ (3)$$

where $$p = a/b. \qquad \ldots \ (4)$$

Combining Eqs. (2) and (3), the dimensions of the target molecule is given by

$$b = \frac{7.5 \times 10^3}{(D_d p\sigma)^{1\cdot 3}} \ \text{A} \qquad \ldots \ (5)$$

If σ be assumed as 1.33 for protein

$$b = \frac{6.81 \times 10^3}{(D_d p)^{1/3}} \ \text{Å} \qquad \ldots \ (5a)$$

The effect of hydration is to increase the target dimensions by an additional thickness of water, from which the radicals can diffuse to the target and inactivate it. If it is assumed that in the wet condition of irradiation, each target molecule is surrounded by an uniform layer of water of thickness ρ Å, then the volume of this water film is given by

$$v_\omega = \frac{4\pi}{3}\,[(a+\rho)(b+\rho)^2 - ab^2] = \frac{4\pi}{3}\,[\rho^3 + \rho^2 b(2+p) + \rho b^2(1+2p)]$$

Replacing b from Eq. 5(a)

$$v_\omega = \frac{4\pi}{3}\,[\rho^3 + 6.81 \times 10^3 . \frac{2+p}{p^{1/3}} \cdot \frac{1}{D_d^{1/3}}\,\rho^2 + 4.63 \times 10^7\,\frac{1+2p}{p^{2/3}} \cdot \frac{1}{D^{2.3}}\,\rho] \quad \ldots \ (6)$$

If Y is the number of radicals formed per primary ionization in water and q is the probability of reaction between the radicals and the target molecules, then increase in the reaction probability per primary ionization, due to the presence of this water layer, is given by

$$\Delta V = \frac{4\pi}{3} Yq \left[\rho^3 + 6.81 \times 10^3 \cdot \frac{2+p}{p^{1/3}} \cdot \frac{1}{D_d^{1/3}} \rho^2 + 4.63 \times 10^7 \cdot \frac{(1+2p)}{p^{2/3}} \cdot \frac{1}{D_d^{2/3}} \rho \right] \quad \cdots \quad (7)$$

Due to this increase in the sensitive volume, the 37 per cent survival dose in the wet condition is smaller than that in the dry condition and the surviving fraction S is given by

$$S = \exp{-I} \left[V\sigma + \frac{4\pi}{3} Yq \left(\rho^3 + 6.81 \times 10^3 \cdot \frac{2+p}{p^{1/3}} \cdot \frac{1}{D_d^{1/3}} \cdot \rho^2 \right. \right.$$

$$\left. \left. + 4.63 \times 10^7 \cdot \frac{1+2p}{p^{2/3}} \cdot \frac{1}{D_d^{2/3}} \cdot \rho \right) \right] \quad \cdots \quad (8)$$

where I is the total number of primary ionizations per cc of unit density material and $\sigma = 1.33$.

If D_w and D_d be the 37 per cent survival doses in the wet and in the dry conditions respectively then from Eq. (2)

$$\Delta V = 1.76 \times 10^{12} \left[\frac{1}{D_w} - \frac{1}{D_d} \right] \quad \cdots \quad (9)$$

$$= \frac{1.76 \times 10^{12}}{D_d} [K-1] \quad \cdots \quad (10)$$

where $\qquad D_d = KD_w$

Equating (7) and (10) and rearranging terms we obtain

$$\rho^3 + 6.81 \times 10^3 \cdot \frac{2+p}{p^{1/3}} \cdot \frac{1}{D_d^{1/3}} \cdot \rho^2 + 4.63 \times 10^7 \cdot \frac{1+2p}{p^{2/3}} \cdot \frac{1}{D_d^{2/3}} \cdot \rho$$

$$= \frac{4.2 \times 10^{11}}{(D_d Yq)} \cdot (K-1) \quad \cdots \quad (11)$$

or $x^3 + 6.81 \times 10^3 \cdot \dfrac{2+p}{p^{1/3}} \cdot x^2 + 4.63 \times 10^7 \cdot \dfrac{1+2p}{p^{2/3}} \cdot x - \dfrac{4.2 \times 10^{11}}{Yq} (K-1) = 0 \cdots$ (12)

where $\qquad\qquad x = D_d^{1/3} \rho \qquad\qquad\qquad\qquad \cdots$ (13)

This is a general expression giving the values of x as a function of the ratio of the dry to the wet dose (K), the shape factor of the target molecule (p) and the probability of inactivation by radical formation per primary ionization (Yq).

This equation may be solved and x obtained for any particular values of K, p and Yq. ρ can then be directly obtained by using Eq. (13) from X and D_{57} in the dry condition. For quick estimation of x under different specified conditions, the charts, given in Figs. 1 and 2, have been prepared.
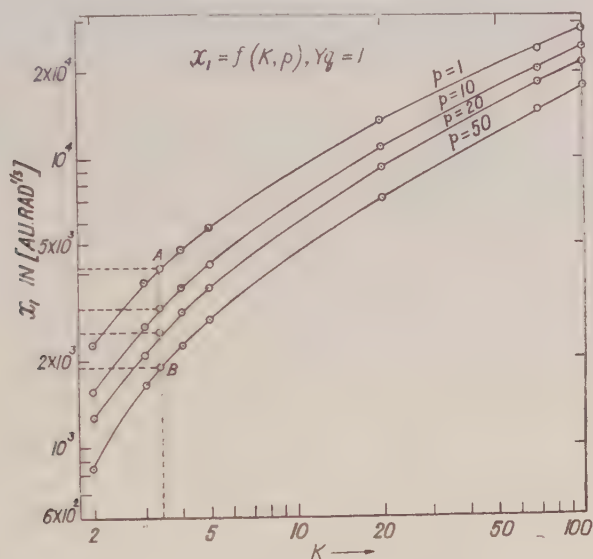
Fig. 1. Variation of x_1 with K, for different values of p.
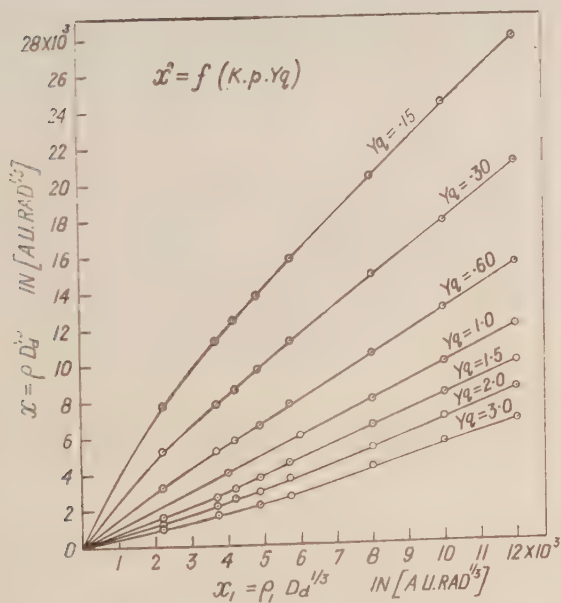
Fig. 2. Variation of x with x_1 for different values of Yq.

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ILLUSTRATION

The diffusion distance may be obtained by successive approximations with the help of Figs. 1 and 2. Fig. 1 gives the approximate values of $x = x_1$ for different values of K and p when $Yq = 1$ i.e., the graph is a plot of the equation

$$x_1{}^3 + 6.81 \times 10^3 \cdot \frac{2+p}{p^{1/3}} \cdot x_1{}^2 + 4.63 \times 10^7 \cdot \frac{1+2p}{p^{2/3}} \cdot x_1 - 4.2 \times 10^{11}(K-1) = 0 \quad (14)$$

With the help of this graph, x_1 can be obtained for any experimentally measured values of dry and wet doses, when the number of effective radicals formed per primary ionization Yq is assumed to be unity. For example, if the dry dose is 20 kilorads and the wet dose 6 kilorads i.e., $K = 3.3$, the values of x_1 are found to be 4.2×10^3, 3.0×10^3, 2.50×10^3 and 1.88×10^3 for $p = 1, 10, 20$ and 50 respectively as shown by the dotted line AB.

Fig. 2 plots the values of x as a function of x_1, for different values of Yq i.e.- it gives the changes in the values of x_1 to x, as the probability of inactivation per primary ionization changes. It is seen from this curve that in the above example, the values of x_1, obtained previously, change to $x = 3.2 \times 10^3$, 2.2×10^3, 1.8×10^3 and 1.4×10^3 respectively as Yq changes from 1 to 1.5. Thus with the help of the graphs given in Figs. 1 and 2, one can obtain the value of $x = D_d{}^{1/3}\rho$ for any combination of p and Yq.

DISCUSSIONS

The method of estimation of diffusion distance developed here is of a very general nature and may be applied to any ellipsiodal target molecule of arbitrary shape and any assumed value of the reaction probability Yq per primary ionization. If the vital molecule is spherical, diffusion distance can be obtained by assuming $p = 1$.

In the case of inactivation of the enzymes various workers (Rajewsky *et al.*, 1957, Hutchinson, 1960) have assumed spherical model. The diffusion distance calculated from the present method given in column 8 of Table I. Column 7 of the Table I gives the value of diffusion distance obtained previously. Inactivation of DNA *in vivo*, has been investigated by Hutchinson *et al.* (1960) who showed that D_{37} for the transforming principle in pneumococus cells was about 3 megarads. Asymmetry of the molecule for the transforming activity was found to be about 40 and diffusion distance calculated from the cylindrical model was 8—10 A.U. The present method gives diffusion distance under this condition as 8 A.U.

The values calculated from the present method seem to be slightly less than those deduced previously. This slight difference is due to the fact that the expression used previously for the calculation of ρ was $\Delta V = 4\pi Yq(\rho b^2 + \rho^2 b)$. For $p = 1$, the general expression (7) differs from this by a term involving ρ^3.

This difference arises from the fact that here an average thickness of water film ρ has been assumed around the vital molecule, thus defining a zone in which all radicals formed has equal probability of inactivating the vital molecule. Absence of ρ^3 term in the expression used previously increased the value of diffusion distance in the case of Invertase, ADH, CoA, Cytochrome C. However in the case of TP, the method used considered the ρ^3 term and the agreement between the two values is therefore excellent.

TABLE I

Diffusion distances from the *in Vivo* radiation inactivation of molecules

Sample	D_{37} in mega-rads.		K	p	Yq per ioniza-tion	ρ Previ-ous in AU	ρ Present in AU	Ref.
	Wet	Dry						
TP (DNA)	1.2	3	2.5	40	1.5	8–10	8	H and A (1960)
Invertase	6	12	2	1	0.15	38	33	
Alcohol dehydro-genase	1.3	28	21	1	2.79	31	25	H (1960)
Co-enzyme A	3	200	67	1	2.70	35	25	
Cyto-chrome C	1	54	54	1	0.3	150	105	R. G and P (1957)

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STUDIES IN K-CAPTURE POSITRON BRANCHING RATIOS-CO⁵⁸*

RATIOS-CO[58]*

M. K. RAMASWAMY[+]

DEPARTMENT OF PHYSICS, THE JOHNS HOPKINS UNIVERSITY
BALTIMORE 18, MARYLAND (USA)

ABSTRACT. One of the methods of determining the Fierz term in Gamow-Teller-transitions is by means of precise determinations of K/β^+ ratio. With this in mind the amount of positron emission in the decay of Co-58 has been measured using coincidence scintillation methods. The measured value is 0.151 ± 0.005. This leads to a $K/\beta+$ ratio of 5.08 ± 0.17 to the 0.810 MeV level in Fe^{58}. On the assumption that the beta transition is pure Gamow-Teller, the Fierz term is computed to be -0.004 ± 0.014.

GENERAL INTRODUCTION

a. *The interaction in beta decay*

The central problem in the theory of beta-decay has been the determination of the nature of the interaction responsible for this decay. In general the interaction can be a linear combination of five types, namely, scalar (S), vector, (V), tensor (T), axial vector (A) and pseudoscalar (P), all satisfying the requirement of relativistic invariance. Beta-Decay can be classified as allowed or forbidden depending on the change in angular momenta and parities of the nuclear states involved. The selection rules permit a further distinction between transitions as Fermi or Gamow-Teller. The selection rules are :

Allowed	$\Delta J = 0$	Fermi
	No	
	$\Delta J = 0, \pm 1$	Gamow-Teller
	No $0-0$	
First forbidden	$\Delta J = 0, \pm 1, \pm 2$	Gamow-Teller
	Yes	
	$0, \pm 1$	Fermi

and so on.

The Fermi transitions involve only the interactions S and V, and the interactions A and T characterize Gamow-Teller transitions. A transition allowed

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by both types of selection rules should therefore involve S, V, A, T and perhaps P. There is strong evidence that the P interaction is unimportant. The fact that transitions obeying both kinds of selection rules are observed indicates that the beta-interaction is an admixture of both Fermi and Gamow-Teller types. It remains to determine the ratio of these interaction strengths. A study of the angular correlation between the electron and the neutrino in an allowed pure transition can be used to distinguish which of the interactions S or V, or A or T is predominant. It is now established from such experiments [Hermansfeldt, (1957, 1958), Alford (1954), Burman (1959)] that the Fermi interaction is mostly V and the Gamow-Teller interaction mostly A. The neutron decay (mixed transition) combined with the O^{14} decay (pure Fermi transition) leads to the determination of the relative strengths of Fermi and Gamow-Teller interactions. The recent Russian measurement (Sosnovski, 1959) of 11.7 ± 0.4, min. for the half life of neutron leads to $(C_{GT}/C_F)^2 = 1.42\pm0.08$.

Considering only pure transitions, Fermi or Gamow-Teller one can expect interference between the two types S and V, or A and T. The possible existence of such terms was first pointed out by Fierz (1937) and hence these terms are called Fierz interference terms. It is the principal objective of the present work to make an estimate of this effect in Gamow-Teller transitions. Such interference is possible in the electron-neutrino angular correlation expression, but because of the difficulties involved in such experiments these terms are often neglected. Interference between A and V in a mixed transition can also occur, but we will not concern ourselves with this here, nor will we treat forbidden transitions.

b. *Fierz interference*

The general expression for the energy distribution of electrons (positrons) in an allowed transition can be written as (Gerhart, 1958)

$$N(W)\,dW = [2\pi^3]^{-1}pW(W_0-W)^2F(Z,W)\zeta(1\pm 2b/W)dW$$

where
$$\xi = 1\!\int\!1\,|^2[k^{-2}(|C_s|^2+|C_s'|^2)+(|C_V|^2+|C_V'|^2)]$$
$$+1\!\int\!\sigma\,|^2(|C_A|^2+|C_A'|^2+|C_T|^2+|C_T'|^2)$$

and
$$\xi b = \pm\gamma[\,|\!\int\!1|^2Re\{k^{-1}(C_SC_V{}^*+C_S'C_V'{}^*)\}+1\!\int\!\sigma\,|^2Re\{(C_AC_T{}^*+C_A'C_T'{}^*)\}]$$

Here the $+$ sign refers to electron, and $-$ to positron emission. The other symbols are explained as follows :

$pW(W_0-W)^2$ is the statistical weight factor which determines, in the absence of the coulomb field, the sharing of energy between the electron and the neutrino.

$F(Z,W)$ is the coulomb field factor which represents the effect of nuclear charge on the emitted electron

p is the momentum of the electron

W is the energy of the electron in relativistic units

W_0 is the maximum energy of the electron or positron

$$k = \int 1 / \int \beta$$

where $\int 1 =$ the scalar matrix element

$\int \beta =$ the vector matrix element

$k = 1$ only if the motion of the nucleons is non-relativistic, since in this case $\beta = \gamma_4 = 1$.

Putting $k = 1$ we get

$$b = \gamma \left[\frac{R_e(C_S C_V{}^* + C_S{}' C_V{}'{}^*) \,|\int 1\,|^2 + R_e(C_A C_T{}^*}{(|C_S|^2 + |C_S|^2 + |C_V|^2 + |C_V{}'|^2) \,|\int 1\,|^2} \right.$$

$$\left. \frac{+ C_A{}' C_T{}'{}^*) \,|\int \sigma\,|^2}{+ (|C_A|^2 + |C_T|^2 + |C_A{}'^2 + |C_T{}'^2) \,|\int \sigma\,|^2} \right]$$

is called the Fierz interference term. Here $\gamma = \sqrt{1 - (\alpha Z)^2} \simeq 1$ represents the screening effect due to the atomic electrons.

$C_i = S, V, A, T =$ is the coupling constant for parity conserving interaction

$C_i{}' = S, V, A, T =$ is the coupling constant for parity non-conserving interaction.

The complex conjugation on the coupling constants represents the possibility of time reversal non-invariance in the beta-decay process.

An immediate consequence of $b \neq 0$ is that the spectral shape of an allowed transition will deviate from the statistical shape because of the inverse dependence on W through b. One way of seeing this deviation experimentally is to plot the form factor

$N(W)/F(Z, W) \, pW(W_0 - W)^2$ as a function of W. From this kind of analysis the limits set on b_{GT} are $-0.09 \leqslant b_{GT} \leqslant 0.20$. Because of the weak dependence on W such deviations are rather hard to detect. Further the analysis has so far been generally restricted to Gamow-Teller transitions only. Recently, Daniel (1958) has applied this method to estimate the Fierz term in the decay of N^{13} ($1/2^- - 1/2^-$). He obtained $b_F = 0.14$ using the O^{14} ft value to evaluate the Fermi part of the matrix element.

Integrating expression (1) over the allowed spectrum, we obtain

$$(2) \qquad\qquad 2\pi^3 (ft^{-1}) \ln 2 = \xi + \xi b <W^{-1}> \qquad\qquad (2)$$

where $f = \int_1^{W_0} F(Z, W) pW(W_0 - W)^2 dW$ is the so-called Fermi function and

$f^{-1} \int_1^{W_0} F(Z, W) p(W_0 - W)^2 dW = <W^{-1}>$ is the expectation value of W^{-1} over the

allowed spectrum.

Thus a consequence of $b \neq 0$ is that the ft values will depend on W^{-1}. From a plot of $2\pi^3 [ft |1|^2]^{-1} \ln 2$ *vs* $2\gamma |\int 1|^2 < W^{-1}>$ which should give a straight line provided $k = 1$ and the matrix elements remain the same. Gerhart (1958) finds from an analysis of data for 0-0. No (Fermi) transitions — O^{14}, Al^{26} and Cl^{34}, that

$$b_F = \gamma \; \frac{Re(C_S C_V{}^* + C_S{}' C_V{}'^*)}{|C_S|^2 + |C_S{}'|^2 + |C_V|^2 + |C_V{}'|^2} = 0.00 \pm 0.12$$

the chief uncertainty being due to the assumption regarding k. (Recently Altman and MacDonald (1958) have considered the effect of coulomb and relativistic corrections to the evaluation of the Fierz term and conclude that the corrections are within experimental uncertainties.) The matrix elements were evaluated by Gerhart on the basis of charge independence of nuclear forces.

Another fruitful approach for the evaluation of b has been the method of K-capture to positron branching ratios first exploited by Sherr and Miller (1954). In the following section we will describe the information that can be derived from a study of K/β^+ ratios and in particular about the Fierz term.

c. *K-Capture positron branching ratios*

The study of the shapes of beta-spectra together with the ft values and the shell model (to determine parities) has been very useful in classifying transitions as to the order of forbiddenness. When, however, between two nuclear states enough energy is available both for K-capture and positron emission, a useful quantity that can be measured is the K-capture positron branching ratio. In fact. it was one of the early triumphs of the Fermi theory of beta-decay that the K-capture mode of decay was observed as predicted. A measurement of the K/β^+ ratio can be used to find the energy difference between two nuclear states if it is known otherwise that the transition is allowed. However, it is observed (Zweifel, 1957) that all allowed shaped transitions (most first-forbidden transitions) have allowed branching ratios also. Thus it is not possible to determine whether an allowed shape transition is indeed allowed. without a knowledge of the parity change. However, the K/β^+ ratio does show a detectable change for unique first forbidden and higher transitions intensified with increasing order of forbiddenness (Brysk, 1958). These latter transitions can probably be much more easily identified on the basis of the shape of the positron spectrum and life-time. In such cases K/β^+ ratios can only serve as an additional check on the assignment. However. the chief virtue of measurement of K/β^+ ratio for supposedly pure transitions is that it lends itself to the estimation of small-order effects in beta-decay such as the Fierz term. Consider a pure transition, say, a Gamow-Teller transition. Then for this transition the probability for positron emission is

$$P_+ = \frac{1}{2\pi^3} \int_1^{W_0} F(Z, W) p W (W_0 - W)^2 \xi (1 - 2b/W) dW$$

where the varius quantities have already been defined. (Note that the terms involving C_S and C_V are set equal to zero.)

The probability for K-capture to the same state can be written as

$$P_K = \frac{1}{4\pi^2} \ (W_0 + W_k)^2 g_k^2(R) \ \xi(1 + 2b)$$

where $g_k^2(R) = \dfrac{1+\gamma}{2\Gamma(2\gamma+1)} \ R^{2\gamma-2}(2\alpha Z_{eff})^{2\gamma+1}$ is the Dirac radial function,

$W_0 =$ total energy available for the transition in $m_0 c^2$ units,

$W_K = \gamma \simeq \sqrt{1 - \alpha^2 Z^2}$

So that the ratio of K-capture to positron emission becomes

$$P_K/P_+ = \frac{(1/4\pi^2)(W_0 + W_k)^2 g_k^2(R)\xi(1+2b)}{(1/2\pi^3) \int_1^{W_0} F(Z, W)pW(W_0 - W)^2 dW\xi(1 - 2b/W)} = R \qquad \qquad .. \quad (1)$$

If the Fierz interference term were zero, then putting $b = 0$, we get

$$(P_K/P_+)_{b=0} = \frac{(1/4\pi^2)(W_0 + W_k)^2 g^2_k(R)}{1/2\pi^3 \int_1^{W_0} F(Z, W)pW(W_0 - W)^2 dW} = R_0 \qquad \qquad .. \quad (2)$$

Dividing Eq. (2) by (1), we obtain

$$R/R_0 = \frac{1 + 2b}{[1 - 2b < W^{-1} >]} \quad \text{where} < W^{-1} > \text{has already been defined.}$$

$$\therefore \qquad \qquad b = \frac{R/R_0 - 1}{2[1 + R/R_0 < W^{-1} >]}$$

Thus a measurement of R can be used to evaluate b. It should be noted that the matrix elements cancel out in the ratio.

Before comparing the theoretical K/β^+ ratio with the observed value, correction for the finite size of the nucleus and screening of the positron and the bound K-electron have to be made. Further, if the measured quantity is the total electron-capture, then correction for capture from higher shells has to be made to obtain the K-capture alone.

For allowed transitions the finite size correction has been shown to be negligible (Zweifel, 1957). The screening correction, on the other hand, is not insigni-

ficant. Recently Perlman, Welker and Wolfsberg (1958) have evaluated the effect of screening on the positron wave function and have given in graphical form the ratio of screened to unscreened values. For most Z values of interest the screening on the K-electron is taken into account by putting $Z_{effective} = Z_k$ -0.3. Zweifel (1957) has evaluated the deviation of the actual Z_{eff} from this Slater screening. Regarding correction for capture from higher shells, only L-capture is important for most cases of interest. (At high Z, M-capture also becomes important.) Correction for L-capture is obtained by using L/K ratios given in graphical form by Rose and Jackson (1949).

We have applied the K/β^+ ratio technique for the decays of Ga[68], Co[58] and Na[22], all pure Gamow-Teller emitters, to obtain the Fierz interference term. The results on Ga[68] have been reported (Ramaswamy, 1959a) briefly at the Cambridge meeting of the American Physical Society, and published elsewhere (Ramaswamy, 1959b).

INTRODUCTION

72 day Co-58 decays by electron capture and positron emission to the 0.810 MeV level in Fe-58 followed by a gamma-ray of this energy to the ground state. Besides, there is a weak electron-capture branch (2%) to the second excited state at 1.63MeV. This level de-excites itself predominantly by the emission of a gamma ray of 0.820 MeV to the 0.810 MeV level and partly by the emission of a gamma ray of 1.63 MeV to the ground state of Fe-58. The decay scheme as given by Frauenfelder *et al.* (1956) is reproduced in Fig. 4. The end-point of the positron spectrum is measured to be 0.472 ± 0.006 MeV (King, 1954). No positron emission to the 0^+ ground state of Fe-58 has been observed. The spin of 0.810 MeV level is 2^+ from systematics of even-even nuclei (Scharff-Goldhaber, 1953). The spin of the second excited state at 1.63 Mev has been assigned 2^+ from angular correlation studies. This is consistent with the presence of a cross-over gamma transition to the 0^+ ground state. The decay of Co-58 to the 2^+ states in Fe-58 and the absence of transition to the 0^+ ground state suggest a spin of 2^+ or 3^+ for Co-58. The spin has been directly measured to be 2 by Dobrov and Jeffries (1957) by means of paramagnetic resonance experiments. The assignment of 2^+ to Co-58 makes the beta transition to the 0.810 MeV level allowd by both Gamow-Teller and Fermi selection rules ($\Delta J = 0$, No). However, recent nuclear orientation experiments of Dagley *et al.* (1958) have shown that the angular distribution of the 0.810 Mev gamma ray is consistent only with the beta transition being pure Gamow-Teller, the amount of Fermi admixture being 0.005 ± 0.003. Thus the measurement of electron capture to positron branching ratio to the 0.810 MeV level becomes of obvious interest from the point of view of determining the Fierz term.

Good *et al.* (1946) and Cook and Tomnovec (1956) have measured the ratio of total electron capture to positron emission in the decay of Co-58 to be 5.9 ± 02.

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When account is taken of the weak electron capture branching to the 1.63 MeV level, the K/β^+ ratio to the 0.810 MeV level becomes 5.8 ± 0.2. This result was obtained by comparison of the intensities of the annihilation radiation and the 0.81 MeV gamma ray, and by a knowledge of the efficiencies. After the work to be described on Co-58 had been completed and briefly published by the author (Ramaswamy, 1958), the work of Konijn et al. (1958) on the same subject has come to attention. By using beta-gamma coincidence technique these workers determined the ϵ/β^+ ratio to be 5.67 ± 0.14.

Neglecting the weak electron-capture branch ($\sim2\%$) to the 1.63 MeV level for the moment, the fraction of positrons in the decay of Co-58 can be expressed as $f_+ = \beta/2c\sigma$, where c is the singles counting rate for the 0.810 gamma ray, β is the coincidence rate between the 0.810 MeV gamma ray and the annihilation radiation, and σ is the efficiency for detecting the annihilation radiation. The value of f_+ when corrected for the presence of the weak branch will give the desired ϵ/β^+ ratio to the 0.810 MeV level.

EXPERIMENTAL

Through the courtesy of Dr. R. W. Hayward of the National Bureau of Standards, Co-58 source was made available for studies. Unfortunately this source contained an appreciable Co-60 impurity. Co-58 was evaporated onto a 0.0003″ mylar foil and sealed with cellophane. The sandwich was then squeezed between two lucite slabs each 1.3 mm thick and 1 cm square. The whole assembly was then sealed with black tape. Thus the positrons from Co-58 (0.470MeV) were completely stopped. The 0.810 MeV gamma ray was detected in a 2″ cube NaI(TI) crystal and the annihilation radiation was detected in a $1\frac{1}{2}″\times1″$ NaI(TI) crystal. Source to detector distance of 1″ to $1\frac{1}{2}″$ was used. A typical singles gamma spectrum measured in the 2″ cube crystal is shown in Fig. 2. Besides the annihilation radiation and the 0.810 MeV gamma ray belonging to Co-58, gamma rays at 1.17 and 1.33 MeV are also prominently seen. The 1.63 MeV gamma ray of Co-58 is too weak to be seen, and no effort was made to observe it. In order to determine the number of counts in the 0.810 MeV photopeak, it is necessary to subtract the Compton background due to Co-60 gamma rays. In order to do this a pure Co-60 source was substituted and its spectrum was carefully normalized to that of Co-58, 60. The dotted curve in Fig. 2 shows the normalized spectrum. For the coincidence measurements a single channel analyzer was set on the photopeak of the annihilation radiation and the spectrum in coincidence was obtained by gating the 20-channel analyzer with the annihilation radiation. The coincidence spectrum thus obtained is shown in Fig. 3. It is observed that the coincident 0.810 MeV gamma ray is superposed on a rather high background due to Co-60. In order to estimate and subtract this background, a coincidence spectrum was taken by replacing Co-58 by Co-60 and the spectrum normalized to the Co-58 spectrum. The resulting background was thus subtracted.
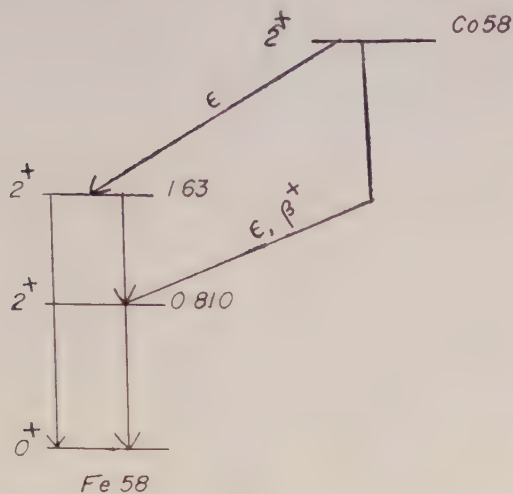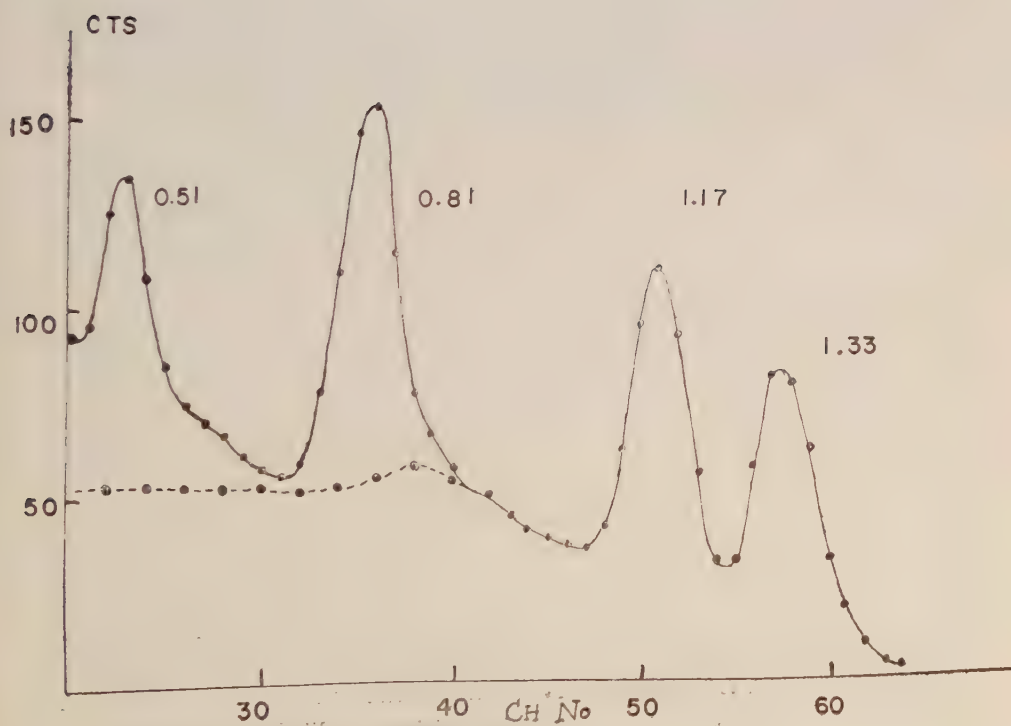
Fig. 1 ,

Fig. 2 .
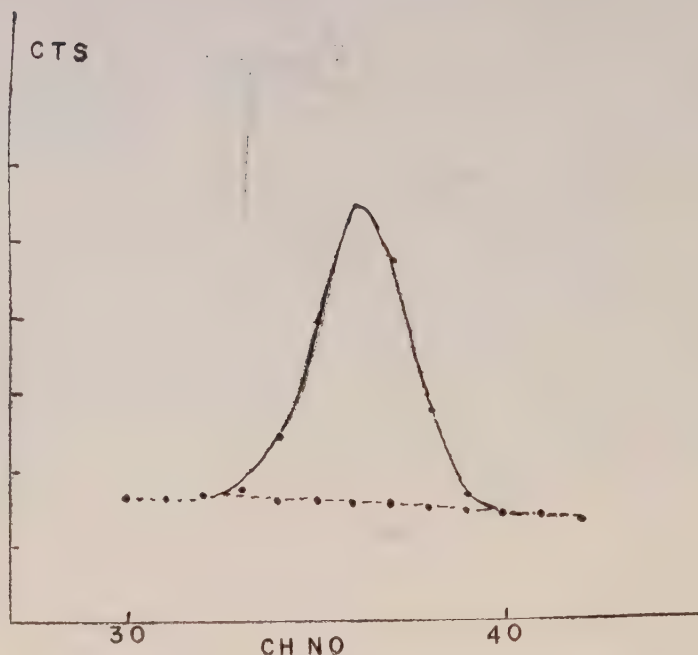
Fig. 3 .

In order to check on the reliability of this procedure, the 0.810 MeV gamma ray was measured in triple coincidence with the two annihilation quanta. From this it was concluded that the background had been correctly estimated. The accidentals were about 10 per cent of true coincidences in the doubles spectrum.

In order to determine σ, the efficiency for detecting annihilation radiation initially a calibrated Na^{22} source (accurate to 3%) was used. By measuring the area under the photopeak and knowing the source strength one could compute the efficiency. A more accurate efficiency determination was made as follows: A N^{13} source (a pure positron emitter of 10 minutes half life) was produced by bombarding a 2 mil polyethelene foil for 10 minutes with 1 MeV deuterons at the Johns Hopkins University Van de Graaff generator through the courtesy of O.N. Rask. After the bombardment the foil was cut into a tiny piece approximating the dimensions of the Co-58 source and sandwiched between two freshly cleaved NaI(TI) crystals 1.2 mm thick and 1 cm square, and mounted in the same geometry as the Co-58 source. The beta spectrum observed in this system is shown in Fig. 4. The energy calibration of the counter was made after the N^{13} source was dead by using external gamma ray sources of Co^{57} (0.123 MeV), Cs^{137} (0.661 MeV) and Na^{22} (1.28 MeV). A Fermi plot of the spectrum is shown in Fig. 5. It has an end-point of 1.16 ± 0.05 MeV, in good agreement with the value of 1.20 MeV (Scharff-Goldhapper, 1953). By following the decay of the activity for 3 half-lives, it was concluded that no impurities were present. Under the conditions of the bombardment, no other impurities were likely to be formed.
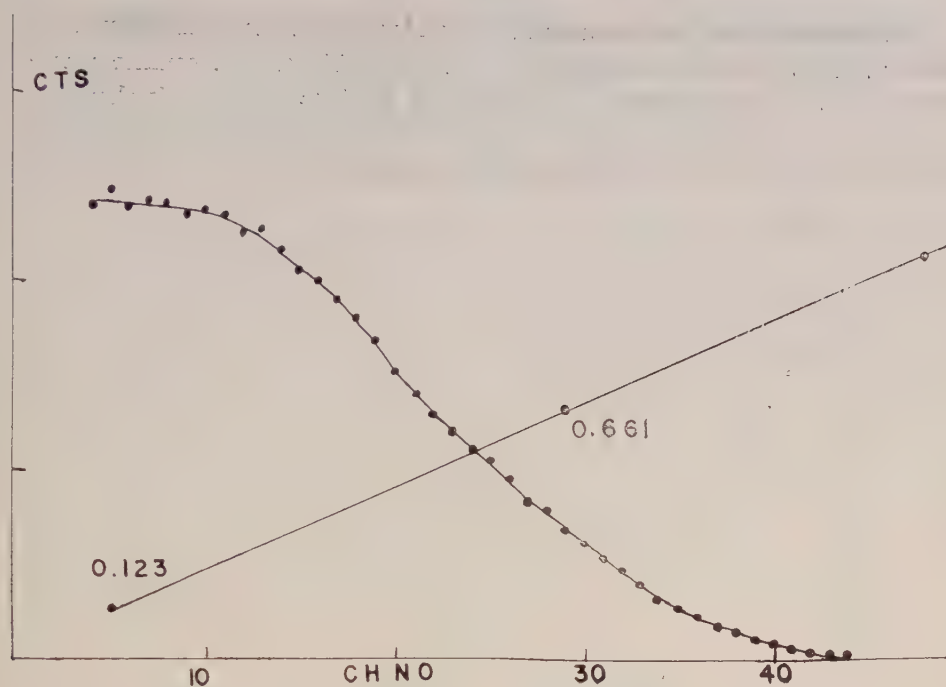
Fig. 4.
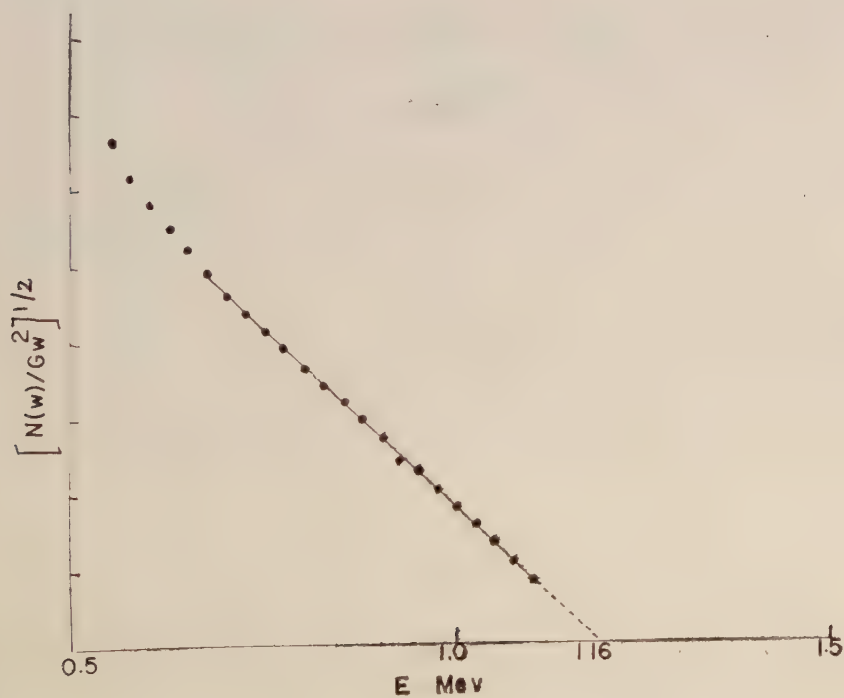
Fig. 5.

The beta-spectrum was measured in coincidence with the annihilation radiation photopeak which was detected by the same $1\frac{1}{2}'' \times 1''$ NaI counter whose efficiency was to be determined. A portion of the beta spectrum is shown in Fig. 6. The efficiency for detecting the annihilation radiation is simply the ratio of the beta-spectrum in coincidence and in singles when corrected for decay.
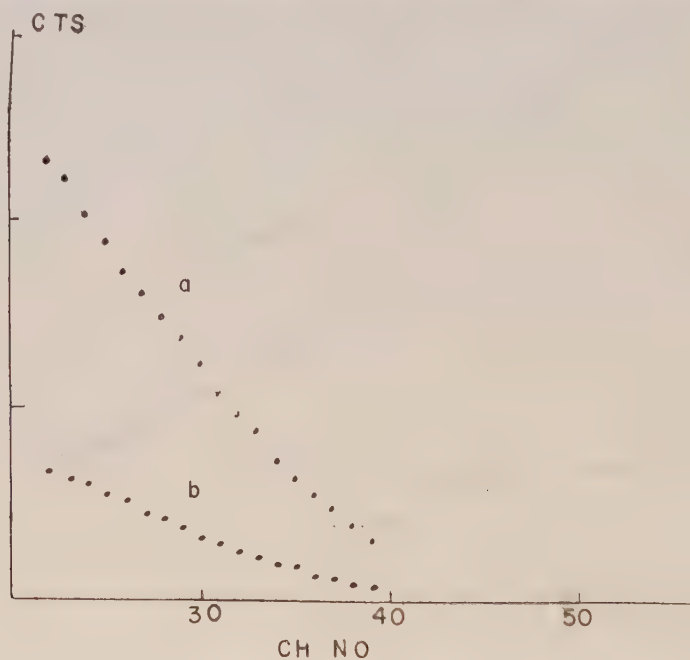
Fig. 6.

Further, since the crystal source was mounted on a light pipe, a correction for the absorption of the 0.511 MeV gamma ray has to be made. This is of the order of 3.7 %. Since the positrons from Co^{58}(0.470MeV) and those from N^{13} (1.2 MeV) have different ranges in lucite and NaI respectively used to annihilate them, one might think that a correction for solid angle has to be made. However, the range of 0.470 MeV positrons of Co^{58} in lucite is 1.4 mm and that of 1.2 MeV positrons of N^{13} in NaI (Tl) is 1.16 mm. The actual thickness used to annihilate the positrons were 1.3 and 1.2 mm respectively. A source to detector distance of 25 mm was used. In view of these circumstances the solid angle correction is less than 1%.

RESULTS

Table 1 lists the results obtained. The uncorrected f_+ is 0.147 ± 0.005. Refering to the Co-58 decay scheme (Fig. 1), it is seen that $1\frac{1}{2}\%$ of the 0.810 MeV gamma rays arise from the 1.63 MeV level, and another $1\frac{1}{2}\%$ arise from cascading to the ground state. The uncorrected f_+ has therefore to be multiplied by 0.03 to get the corrected value of f_+. In order to obtain the amount of elec-

tron-capture to the 0.810 MeV level, it should be noticed that 2% of the Co-58 transitions lead to the 1.63 MeV level. Hence $\epsilon = 0.98 - 0.151 \pm 0.005$. Thus the ϵ/β^+ ratio to the 0.810 MeV level is computed to be 5.49 ± 0.18. The error introduced in the value of 2% for the branching is very small.

DISCUSSION

The ϵ/β^+ ratio computed above has to be corrected for 8% *L*-capture to give (Gerhart, 1958) the value K/β^+ ratio. The value so obtained is 5.08 ± 0.17. The theoretical value is $5.15 - 0.24$ corresponding to maximum beta energy of $0.472 - 0.006$MeV. Thus our value is in excellent agreement both with theory and with previous measurements. As before, the Fierz term is computed from the expression

$$ b = \frac{R/R_0 - 1}{2[1 - R/R_0 < W^{-1}>]} $$

For Co-58 $< W^{-1}> = 0.76$ corresponding to $W_0 = 1.924$.

∴ $b = -0.004 \pm 0.014$

TABLE I

Summary of results on Co[58]

(For symbols see text)

$c = 91.00 \pm 1.12$ cps

$\beta = 0.242 + 0.003$

σ : (a) from Na[22]

Source strength $= N_0 =$ no. of positrons/min $= (3.16 \pm 0.10) \times 10^5 \beta^+$/min

$a =$ no. of cts in the 0.511 photopeak $= 47.0 \pm 0.0$ cps

$\sigma = a/N_0 = (8.92 \pm 0.33) \times 10^{-3}$

      (b) from N[13]

$N_{\beta,0.5} = 358.0 + 6.0$ cpm

$N_\beta = 23200 + 150$ cpm

$\sigma = \frac{1}{2} \frac{N_\beta 0.5}{N_\beta} = (9.02 \pm 0.18) \times 10^{-3}$

f_+ (uncorrected) $= \beta/2c\sigma = 0.147 \pm 0.005$

f_+ (corrected) $= (0.147 \pm 0.005) \, 1.03 = 0.151 \pm 0.005$

$\epsilon = 0.980 - f_+ = 0.829 \pm 0.005$

$\epsilon/\beta+ = \dfrac{0.829 \pm 0.005}{0.151 \pm 0.005} = 5.49 \pm 0.18$

$L/K = 0.08$

∴ $K/\beta^+ = 5.08 \pm 0.17$

CONCLUSIONS

The fraction of Co-58 decays by positron emission has been measured by coincidence methods using NaI crystals. The value is 0.151 ± 0.005. This value leads to a K/β^+ ratio of 5.08 ± 0.17 for the beta transition to the 0.810 MeV level

The theoretical ratio is 5.15 ± 0.24. The Fierz term is computed to be -0.004 ± 0.014. It is rather striking that the theoretical value of K/β^+ ratio has a larger error than the measured value.

It follows then that the Fierz interference term is extremely small. Unfortunately Co-58 is not the best case, since a small admixture to Fermi component in the beta transition may invalidate the conclusions reached so far. However, if it turns out, as is likely, that the Fermi component is zero, then it may be worth while to measure the end-point of the positron spectrum more accurately. The smallness of the Fierz term has been conclusively shown from Na^{22} decay (Ramaswamy, 1959c)

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SCATTERING OF ELECTRON BY EXCITED
HELIUM ATOM

MRS. TARA BHATTACHARYYA

DEPARTMENT OF THEORETICAL PHYSICS,

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, JADAVPUR, CALCUTTA-32

ABSTRACT. Born's first approximation formula has been applied here to calculate the differential cross section of scattering of an electron by an excited helium atom. It is found that the cross section of scattering of electrons of 700 eV energy by excited He atom is very nearly the same as that by screened He atom ; the cross section of scattering of the same by bare He nucleus is slightly greater than both of them. However, the experimental cross section for ordinary He is considerably larger than these three theoretical results at angles above 80°, whereas at angles below 70°, the experimental values are less than all the theoretical values.

INTRODUCTION

Various models have been proposed to take into account the screening effect of the two electrons surrounding the nuclear charge. To calculate the above screening. Hylleraas (1929) has taken the wave function of the Schrödinger equation to be a product of two wave functions in the $1s$ state with $Z = \frac{27}{16}$, Z being the nuclear charge value.

Huzinaga (1960), on the other hand, has taken symmetrized product of two wave functionsa in $1s$ state with two different Z values.

In the present paper we propose to study the problem of scattering of electrons if the target atoms are already excited. In actual experimental conditions, the target atoms are also excited by inelastic collisions, so that there is always a certain fraction of the number of atoms which are in excited states ; it is worth while to see how the scattering is effected by the excited states of the target atoms. Here we are considering one of the electrons to be in its $1s$ state and the other in $2s$ state.

MATHEMATICAL RESULTS

The potential function of atom having two electrons is given by

$$V = -e^2 \int\limits_{\tau_1=0}^{\infty} \int\limits_{\tau_2=0}^{\infty} \psi * \left\{ \frac{2}{r} - \frac{1}{|r-r_1|} - \frac{1}{|r-r_2|} \right\} \psi \, d\tau_1 \, d\tau_2 \qquad \ldots \quad (1)$$

where the co-ordinates of the two electrons of the atom are denoted by r_1 and

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r_2 and r is the co-ordinate of the incident electron with the nucleus as the origin. ψ is the wave function of the system and is taken to be

$$\psi = \frac{N}{\sqrt{2}} \{R_1(r_1) R_2(r_2) + R_1(r_2) R_2(r_1)\}$$

where

$$R_1 = \left(\frac{Z_1}{a_0}\right)^{\frac{3}{2}} 2e^{-\frac{Z_1 r}{a_0}}$$

$$R_2 = \left(\frac{Z_2}{2a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Z_2 r}{a_0}\right) e^{-\frac{Z_2 r}{a_0}}$$

and the normalization factor N is given by

$$N^2 = \frac{1}{4\pi^2 \left\{1 + 8Z_1{}^3 Z_2{}^3 \left(\frac{2}{2Z_1 + Z_2}\right)^8 (Z_1 + Z_2)^2 \right\}}$$

Substituting (2) in (1) we obtain for V the following expression

$$V = -(4\pi)^2 N^2 e^2 \left[\frac{2}{r} \left\{ 8Z_1{}^3 Z_2{}^3 \left(\frac{2}{2Z_1 + Z_2}\right)^8 (Z_1 - Z_2) \right\} \right.$$

$$+ \left(\frac{1}{r} + \frac{Z_1}{a_0}\right) e^{-\frac{2Z_1 r}{a_0}} + \left(\frac{1}{r} + \frac{3Z_2}{4a_0} + \frac{1}{4}\frac{Z_2{}^2}{a_0{}^2} r + \frac{1}{8}\frac{Z_2{}^3}{a_0{}^3} r^2\right) e^{-\frac{Z_2 r}{a_0}}$$

$$+ e^{-\frac{r}{2a_0}(2Z_1 + Z_2)} \left\{4Z_1{}^3 Z_2{}^3 \left(\frac{2}{2Z_1 + Z_2}\right)^4 (Z_1 - Z_2)\right\} \left\{\frac{2(Z_1 - Z_2)}{2Z_1 + Z_2} r^2 \right.$$

$$\left. - \frac{4Z_2 a_0 r}{(2Z_1 + Z_2)^2} + \frac{8a_0{}^2(2Z_1 - 3Z_2)}{(2Z_1 + Z_2)^3} - \frac{8(Z_1 - Z_2)}{r}(2a_0)^3 \frac{1}{(2Z_1 + Z_2)^4}\right\}\right] \quad \cdot \cdot \quad (3)$$

To calculate the differential scattering cross section $\sigma(\theta)$ which is $|f(\theta)|^2$ we opply the Born approximation method in which $f(\theta)$ is given by

$$f(\theta) = \frac{8\pi^2 m}{h^2} \int_0^\infty \frac{\sin kr}{hr} V(r) r^2 \, dr \qquad \cdot \cdot \quad (4)$$

Substituting the value of V from Eq. (3) in Eq. (4) we obtain

$$f(\theta) = \frac{2me^2}{\hbar^2 k^2} \; \frac{1}{\left\{ 1 + 8Z_1^3 Z_2^3 \left(\frac{2}{2Z_1 + Z_2} \right)^8 (Z_1 - Z_2)^2 \right\}}$$

$$\times \left[\; 16 Z_1^3 Z_2^3 \left(\frac{2}{2Z_1 + Z_2} \right)^8 (Z_1 - Z_2)^2 \right.$$

$$+ \frac{k^2 a_0^2 (k^2 a_0^2 + 8Z_1^2}{(4Z_1^2 + k^2 a_0^2)^2} - \frac{k^2 a_0^2}{(Z_2^2 + k^2 a_0^2)^4} \{ 7 Z_2^6 + 4 Z_2^4 a_0^2 k^2$$

$$+ 4 Z_2^2 a_0^4 k^4 - a_0^6 k^6 \} - \frac{4 Z_1^3 Z_2^3}{a_0^3} \; \frac{\left(\frac{2}{2Z_1 + Z_2} \right)^4 (Z_1 - Z_3)(2a_0)^4 \, R}{(2Z_1 - Z_2)^4 \{ (2Z_1 + Z_2)^2 + 4k^2 a_0^2 \}} \right] \quad \dots \quad (5)$$

where $R = 4\{ 2(2Z_1 + Z_2)^3 \, ka_0 - 8(2Z_1 + Z_2) k^3 a_0^3 \} \{ 64 Z_1^4 - 16 Z_1^3 Z_2$

$$- 120 Z_1^2 Z_2^2 - 76 Z_1 Z_2^3 - 14 Z_2^4 + 32 Z_1^3 k^2 a_0^2 - 8 Z_2^2 k^2 a_0^2 \}$$

$$+ 2 ka_0 (32 Z_1^2 + 40 Z_1^2 Z_2 + 8 Z_1 Z_2^2) \{ (2Z_1 + Z_2)^4 - 24(Z_2 + 2Z_1) k^2 a_0^2 + 16 k^4 a_0^4 \}$$

If we put $Z_1 = 2$, $Z_2 = 1$, we get

$$f(\theta) \quad = \frac{2a_0}{k^2 a_0^2 \left\{ 1 + 64 \left(\frac{2}{5} \right)^8 \right\}} \left[128 \left(\frac{2}{5} \right)^8 + \frac{k^2 a_0^2 (32 + k^2 a_0^2)}{(16 + k^2 a_0^2)^2} \right.$$

$$\left. \qquad\qquad + \frac{k^2 a_0^2}{(1 + k^2 a_0^2)^4} \left\{ (7 + 4k^2 a_0^2 + 4k^4 a_0^4 + k^6 a_0^6) \right\} \right]$$

In the above we have neglected the contribution of the last term of the expression (5) as it is very small compared with those of the other terms.

DISCUSSIONS

In the table below we have given the numerical values of the differential cross section at different scattering angles for the incident electron energy of 700 ev. For comparison we also give similar values of the differential cross section when the screening due to the electrons is completely neglected. In the third column the experimental values (Hughes, Mac Millan and Webb, 1932) are added.

TABLE I

Energy 700 ev

$|f(\theta)|^2$ in units of 10^{-20} cm^2

θ	$|f(\theta)|^2$ Present result	Coulomb field	Experimental values
57°	17.19	20.25	15.5
72°	8.4	8.8	8.12
87°	4.46	4.7	5.10
102°	2.37	2.88	3.97
117°	1.97	2.00	3.56
132°	1.48	1.53	3.44
147°	0.9	1.25	1.54

From the above table we find that the present theoretical cross section of scattering of electrons of 700 ev energy by excited He atoms is considerably
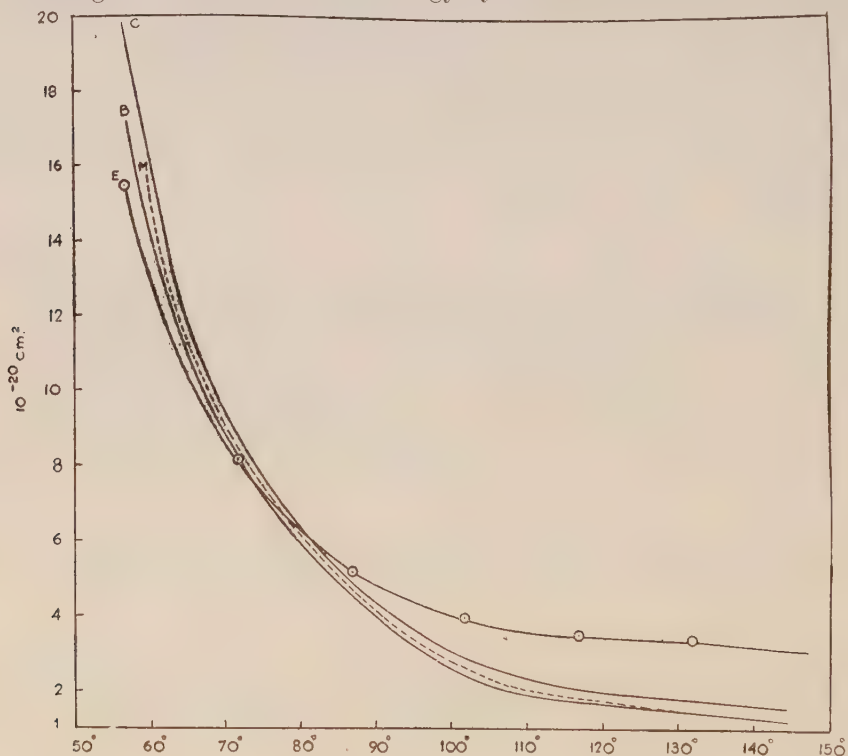

Fig. 1. Differential scattering cross section is plotted against angles in degrees. The curves marked E, B, M and C represent respectively the experimental results and the theoretical results of Bhattacharyya, Mukherji and of coulomb scattering of the bare nucleus.

lower than the experimental cross section of scattering by ordinary He, at large angles of scattering. The theoretical cross section of scattering by screened He atoms in the ground state calculated by the method of Born's first approximation (Mukherjee, 1961) is given in the graph and found to be very nearly the same as the scattering cross section by excited He atoms at angles above 90°, and slightly larger at angle below 90°. The cross section of scattering by bare nucleus calculated by the first Born approximation method is larger than both the theoretical cross sections either by ordinary He atoms or by excited He atoms; this shows that the influence of screening is not so appreciable at this energy of the incident electron. Moreover, the fact that the cross section of scattering even by bare nucleus calculated in the first Born approximation is much lower than the experimental findings at angles greater than 80°, seems to indicate the inadequacy of the first Born approximation and the necessity of taking into account higher order terms of Born series.

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ON THE SINGLET→TRIPLET ABSORPTION IN A FEW POLYSUBSTITUTED BENZENES IN THE VAPOUR STATE*

J. K. ROY

Optics Department,

Indian Association for the Cultivation of Science,
Calcutta-32

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ABSTRACT. The absorption spectra in the near ultraviolet region of ortho-, meta- and parafluorotoluene, m-chlorotoluene, 2, 4-dichlorotoluene and 3, 4-dichlorotoluene in the vapour state at the room temperature and with a path length equivalent to about 7 mm of the liquids have been investigated and compared with those due to equivalent path lengths of the liquids. In the case of 2, 4-dichlorotoluene and 3, 4-dichlorotoluene the spectra have also been photographed with the vapours at about 205°C using a high dispersion spectrograph.

It has been observed that these vapours exhibit continuous absorption starting at different points in the region lying between 26000 cm⁻¹ and 32000 cm⁻¹ and increasing towards longer wavelengths. When the vapours are liquefied the region of absorption shifts towards longer wavelengths, the shift being larger for ortho compounds than for the para compounds, but the long wavelength limit in the spectra of the isomeric molecules in liquid state are almost identical. It has been found that the spectra due to the vapours at different temperatures are identical. These results have been discussed.

INTRODUCTION

The absorption spectra of some substituted benzene and toluene compounds in the vapour state at the saturation vapour pressure of the substances at the room temperature and with a path length of about 18.90 metres were studied recently by Sirkar and Roy (1960) and by Roy (1961). They observed weak continuous structureless absorption spectrum in the near ultraviolet region at large distances on the long wavelength side of the region of absorption due to singlet→singlet transition. They assigned this continuous absorption to singlet→triplet transition in the molecules. It was further observed that the continuous absorption increases considerably in some cases when equivalent path lengths of the substances in the liquid state are used. It was concluded that the increase is due to perturbation by the surrounding molecules of the same kind in the liquid state.

In the previous experiments long path of the vapours at low pressures at the room temperature was used in order to obtain sufficient path lengths of the vapour equivalent to that of the liquid without change of temperature. It was not known whether the continuous absorption spectrum attributed to singlet→triplet transi-

*Communicated by Professor S. C. Sirkar

tion in the molecules is affected by temperature and pressure. It was, therefore, thought worthwhile to study the influence of temperature on the absorption due to the vapour. For this purpose the absorption spectra in the near ultraviolet region in two dihalogen substituted toluenes in the vapour state at the saturation pressures at the boiling points of the liquids and with path lengths of 140 cm have been investigated and compared with those due to equivalent path lengths of the substances in the vapour and liquid states at the room temperature.

The influence of heavy atoms as substituents in the benzene or naphthalene molecule on the singlet→triplet absorption spectrum was investigated by previous authors (McClure, Blake and Hanst, 1954) but it was not definitely known how such an influence changes with the change in position of the substituents in the ring. To find out such changes the absorption spectra of a few halogen substituted toluenes in the vapour state at the saturation pressures at the room temperature have been investigated using a path length about 18.90 metres and compared with the spectra due to the liquids with equivalent path lengths.

EXPERIMENTAL

The substances selected for the present investigation are ortho-, meta- and parafluorotoluene, metachlorotoluene, 2-,4-dichlorotoluene and 3, 4-dichlorotoluene. Orthofluorotoluene of chemically pure quality was obtained from Dr. Theodor Schuchardt, Germany, meta- and parafluorotoluene from Eastman Kodak Co., U.S.A. and metachlorotoluene, 2,4-dichlorotoluene and 3, 4-dichlorotoluene from Fisher Scientific Company, U.S.A. The colourless samples were distilled several times under reduced pressure before being used in the present investigation.

The experimental arrangement for recording the ultraviolet absorption spectra of the substances at the room temperature was the same as that employed in the previous investigations (Sirkar and Roy, 1960; Roy, 1961). The absorption spectra of the substances in the vapour state where photographed first by filling the 18.90 metres long absorption cell with the vapours of the compounds at the saturation pressures at about 24 C. The pressures measured with a differential manometer were found to be about 60 mm, 50 mm and 45 mm of Hg in the cases of the fluorotoluenes, metachlorotoluene and dihalogenated toluenes respectively. The equivalent path lengths of the liquids were 7.4 mm, 6.5 mm and 6.4 mm respectively. In each case an empty cell of length equal to equivalent path length for the liquid was first placed in the path of the beam while the absorption spectrum due to the vapour was recorded with a cell of length 1890 cm. The long cell was then evacuated and the short cell was filled with the pure liquid and the absorption spectrum of the liquid was photographed by the side of the spectrum due to the vapour. An Adam Hilger medium quartz spectrograph giving a dispersion of about 22 A/mm in the 3500 A region was used for this purpose.

The absorption spectra of the substances in the vapour state at temperatures near about the boiling points of the liquids were studied in the cases of 2, 4-dichloro-toluene and 3,4-dichlorotoluene using a 140 cm long Pyrex glass cell fitted with quartz windows. The cell was placed inside a long cylindrical heater and was heated to a temperature slightly above the boiling point of the liquid and another heater was used to heat the liquid contained in a bulb attached through a side tube to the long cell. The temperature of the bulb was raised to the boiling point of the liquid and was kept constant during the experiment. The corresponding path length for the liquid was 7.6 mm in each case. After photographing the absorption spectrum of the vapour, that due to the liquid at the room temperature was photographed on the same film using a cell 7.6 mm long and the same time of exposure. The continuous spectrum due to the incident light was also photographed in order to compare the absorption spectrum of the vapour with the spectrum of the incident light. A Hilger E. 476 automatic quartz spectrograph giving a dispersion of about 8 A/mm in the 3500 A region was used for photographing the spectra of the vapours at high temperature (205°C). Agfa Isopan films backed by metal plates were used to photograph the spectra. Iron arc spectrum was photographed on each spectrogram as comparison. Microphotometric records of the spectrograms were obtained with a self-recording microphotometer made by Kipp and Zonen. The wave lengths in the continuous absorption spectra were measured by drawing a sharp line across the spectrogram in the position of a known iron line in the adjacent iron arc spectrum and comparing the micro-photometric record of the iron arc spectrum with that of the absorption spectrum.

RESULTS AND DISCUSSION

The microphotometric records of the absorption spectra due to pure ortho-fluorotoluene and parafluorotoluene in the liquid and vapour states at room temperature are reproduced in Figs. 1(a)–1(d), those due to pure 2, 4- and 3, 4-dichloro-toluene are reproduced in Figs. 2(a)–2(d). The records due to pure m-fluorotoluene and m-chlorotoluene are reproduced in Figs. 3(a)–3(d) respectively. The micro-photometric records of the absorption spectra due to pure 2, 4- and 3, 4-dichloro-toluene at the high temperature are shown in Figs. 4(a), (b) and 5(a), (b) respectively. The reference line in the records has the wave length 4046A.

It can be seen from Figs. 1, 2, 3 and 4 that the vapours of the substances show continuous absorption in the region 3600 A–3300A and its strength increases rapidly towards shorter wavelengths starting from the long wavelength limit. The position of the long wavelength limit is slightly different for the different compounds. Also the relative positions of the substituents has some influence on the strength of the S→T absorption, as can be seen from a comparison of the records due to ortho- and parafluorotoluene in Figs. 1(a), 1(b), 1(c) and 1(d) and those due to 2, 4-dichlorotoluene and 3, 4-dichlorotoluene shown in Figs. 2(a), 2(b), 2(c) and 2(d). It appears that in the vapour state the strength of absorption
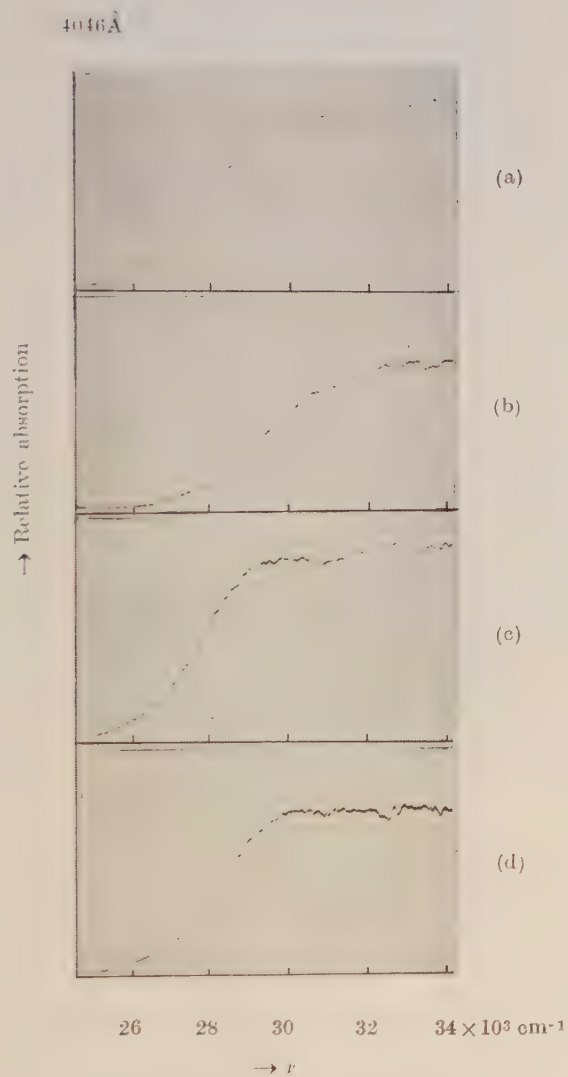
Fig. 1 (a) *o*-Fluorotoluene (liquid)
(b) *o*-Fluorotoluene (vapour)
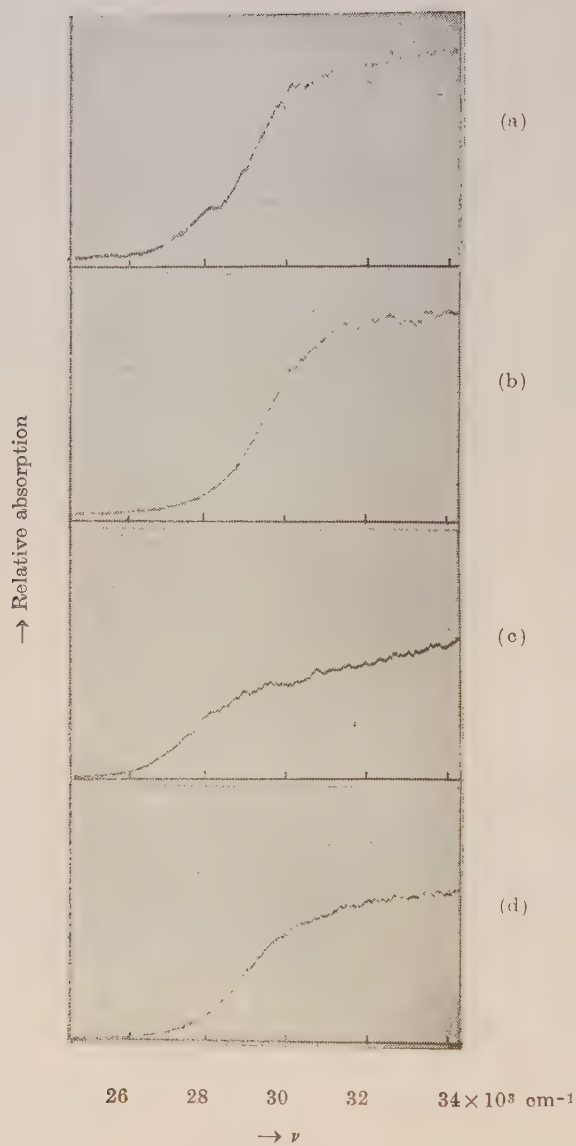(c) *p*-Fluorotoluene (liquid)
(d) *p*-Fluorotoluene (vapour)

J. K. Roy

4046Å

Fig. 2 (a) 2,4-Dichlorotoluene (liquid)

(b) 2,4-Dichlorotoluene (vapour)

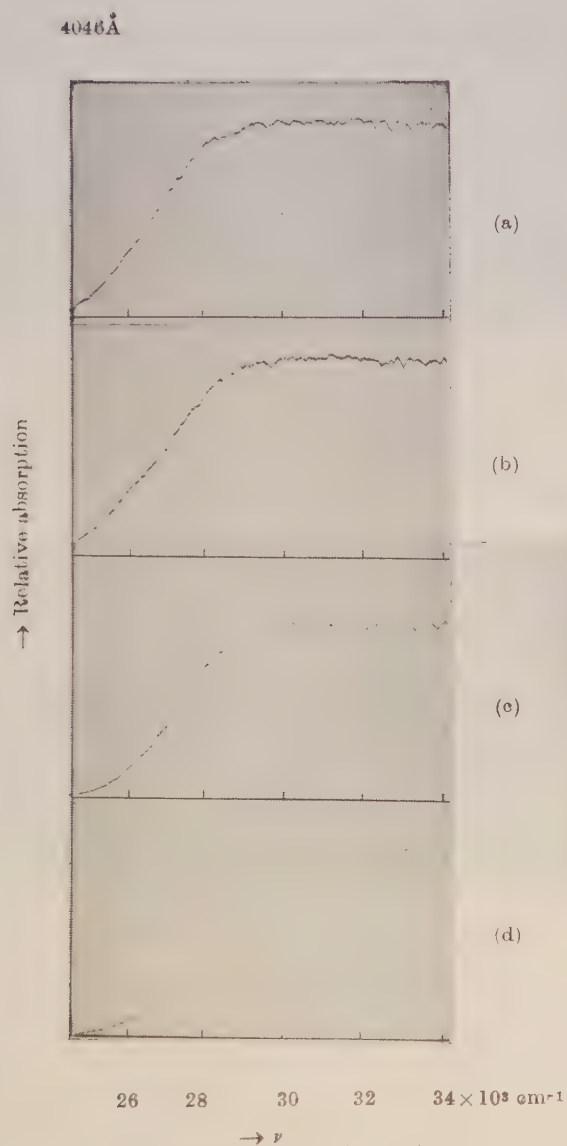(c) 3,4-Dichlorotoluene (liquid)

(d) 3,4-Dichlorotoluene (vapour)

4046Å

Fig. 3 (a) *m*-Fluorotoluene (liquid)

     (b) *m*-Fluorotoluene (vapour)

     (c) *m*-Chlorotoluene (liquid)
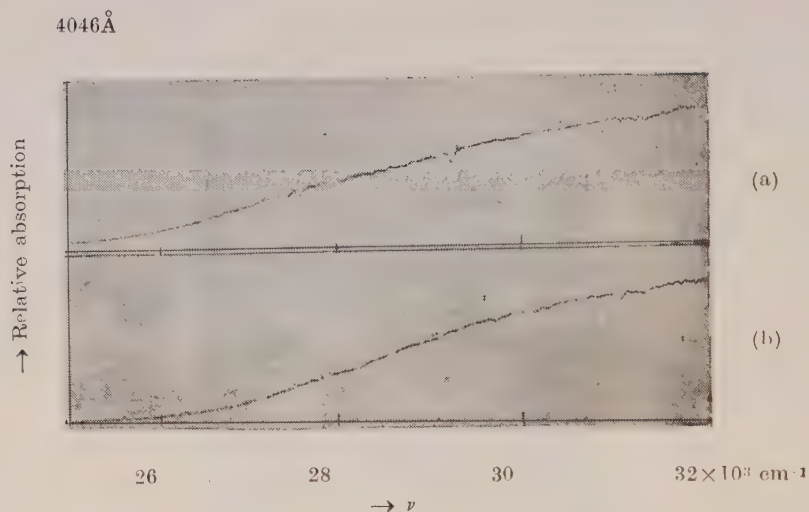
     (d) *m*-Chlorotoluene (vapour)

4046Å

Fig. 4. (a) 2,4-Dichlorotoluene (liquid) at 30°C,
(b) 2,4-Dichlorotoluene (vapour) at 205°C

4046Å

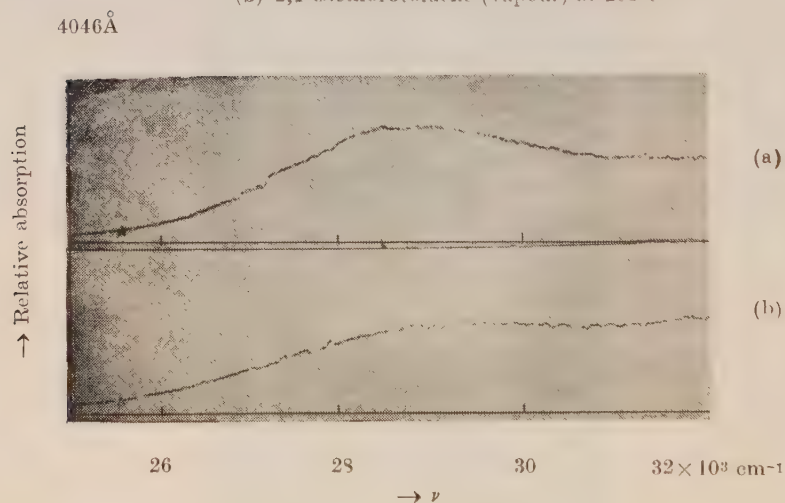Fig. 5. (a) 3,4-Dichlorotoluene (liquid) at 30°C,
(b) 3,4-Dichlorotoluene (vapour) at 205°C

at about 30,000 cm^{-1} is larger in the case of p-fluorotoluene than in the case of the ortho compound, but the increase in the strength due to intermolecular field in the liquid is larger in the latter case than in the former case. Fig. 2 on the other hand shows that absorption due to the 2,4- and 3, 4-dichlorotoluene in the vapour state is almost identical in respect of position and strength, but the increase due to intermolecular field in the liquid is larger in the latter case.

It would be interesting to find out how far the strengths of absorption in the vapours of the different substituted benzene molecules can be explained with the help of vector diagrams which were used by Platt (1951) to explain the singlet→

singlet systems of such compounds. It was shown by Platt that the transition moments due to the substituents CH_3 and halogen atoms have the same sign in the case of singlet→singlet transition. Assuming this to be true for the singlet →triplet transition also, it can be seen from the vector diagrams for trisubstituted benzenes that the resultant transition moments for 2. 4-dichlorotoluene and 3. 4-dichlorotoluene are exactly the same. The curves in Figs. 2(b) and 2(d) show that the strengths of absorption and positions of the region of absorption in the vapours of the two compounds are the same. Again, the vector diagrams for disubstituted benzenes show that the transition moment of the para substituted compound should be larger than that of the ortho substituted compound. The curves in Figs. 1(b) and 1(d) show that the experimental results agree with those deduced from the vector diagrams. Figs. 3(b) and 3(d) also show that the heavier atom chlorine produces a larger transition moment than the lighter substituent atom fluorine both situated at the meta position.

It appears from these results that the substituent atoms make the forbidden transition to the triplet state allowed, but the upper triplet state becomes very broad and diffuse. Probably the perturbation due to the substituent atoms changes the nature of coupling between the spin and orbital angular momentum so that the resultant spin is not quantised and this may explain the continuous nature of the upper state.

It can be seen from the curves reproduced in all the figures that the region of absorption shifts towards longer wavelengths as the vapour is liquefied, the shift being different for the different compounds. It is remarkable, however that the long wavelength limits for the curves due to isomeric molecules with the same substituents are exactly the same. This shows that the perturbation due to the heavy substituent atom in the neighbouring molecule is responsible for the shift of the spectrum. As this effect is exhibited mostly by polar molecules it may not be unlikely that formation of loose dimers takes place in the liquid state and the shift may be partly due to such bond-formation.

Fig. 4 shows that curves due to 2, 4-dichlorotoluene in the vapour state at 205°C and in the liquid state at 30°C. A comparison of the curve due to the vapour at 205 C. Fig. 4(b) with that due to the vapour at 30 C reproduced in Fig. 2(b) shows that the curves are identical. This shows that temperature and pressure have very little influence on the absorption.

The microphotometric records of the spectra due to 3,4-dichloro-toluene in the liquid state at 30 C and in the vapour state at 205 C photographed with the high dispersion spectrograph and reproduced in Fig. 5 show that in both the curves there is a tendency for the formation of a very broad maximum. The centre of the maximum is at about 29200 cm^{-1} in the case of the vapour. The maximum is more prominent in the case of the liquid and its centre shifts to about 28500 cm^{-1}. Such a phenomenon is not exhibited by 2 ,4-dichlorotoluene. This may

be due to overlapping of the singlet→triplet and singlet→singlet systems in the latter case.

It is thus evident from the results for the compounds mentioned above that the absorption due to siglet→triplet transition is continuous with a maximum in some cases and the perturbation due to heavy atoms in the neighbouring mole- cules always shifts the region of absorption towards longer wavelengths.

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AMPLITUDE OF THERMAL VIBRATIONS IN PCl₃, AsCl₃ AND SbCl₃ MOLECULES

T. A. HARIHARAN

DEPARTMENT OF PHYSICS,

KARNATAKA REGIONAL ENGINEERING COLLEGE,

SURATHKAL S. K. (MYSORE STATE)

ABSTRACT. The root mean square amplitudes of vibration of the bond distances during the totally symmetric stretching vibrations have been calculated for the molecules PCl_3, $AsCl_3$, $SbCl_3$ at a temperature of $300°K$. The necessary potential and kinetic energy matrices were worked out using symmetry coordinates corresponding to the two species of vibrations in each case.

INTRODUCTION

The determination of the mean square amplitudes of thermal vibrations of atoms in crystals is of considerable importance in the X-ray crystal structure analysis (James, 1948; Lonsdale, 1948; Cribier, 1953 and Cochran, 1954). In the particular case of molecular crystals Cruickshank (1956) and Higgs (1953, 1955) have shown that the vibrational spectra of the constituent molecules and the normal co-ordinate analysis can be used to determine the contribution to the mean square amplitude of thermal motions of atoms from internal molecular vibrations. In the case of free molecules, accurate interpretation of the precise electron diffraction data makes it necessary to take into account the mean square amplitude of thermal vibrations of the atoms. A simple procedure for calculating these amplitudes has been developed by Morino *et al* (1953) and applied successfully to the molecules C_2F_4 and CH_2F_2. The present investigation follows a similar procedure to calculate the mean amplitudes for the molecules PCl_3, $AsCl_3$ and $SbCl_3$ and the results are presented here.

METHOD OF CALCULATION

The mean square amplitude of thermal vibrations in molecules is given by the well known formula

$$< Q_n^2 > = \frac{h}{8\pi^2 \nu_n} \coth \frac{h\nu_n}{2kT} .$$

where, Q_n represents the normal coordinate.

ν_n the frequency.

T the absolute temperature.

and k the Boltzmann constant.

By making use of appropriate transformation matrices we can determine the mean square amplitudes corresponding to the internal coordinates rather than the normal coordinates. These matrices can be obtained once the proper Wilson's G and F matrices for the molecular vibrations are determined. A simplified procedure has been used by Morino *et al* (1953) and this lies in the approximate expansion of the coth function as

$$\coth x = \frac{1}{x} + \frac{x}{4}$$

This of course involves slight error from the actual expansion but is applicable to frequencies less than 1200 cm^{-1}.

The final relation for the amplitudes corresponding to the internal coordinates R is given by

$$< R_i^2 > = kT(F^{-1})_{ii} + \frac{h^2}{64\pi^2 kT} G_{ii}$$

$$(F^{-1})_{ii} = \frac{F_{ii}'}{det F} .$$

F and G correspond to the Wilson's potential and kinetic energy matrices. Symmetry coordinates can also be used with the appropriate transformation matrices.

The molecules PCl_3, $AsCl_3$ and $SbCl_3$ are known to have a pyramidal structure and they belong to the point group C_{3v}. The vibrational spectra of these have been obtained by several investigators and fairly accurate assignment of the observed frequencies is available. A normal coordinate analysis has been carried out by Howard and Wilson (1934) using four force constants.

In the present case the Wilson's F and G matrices are calculated using a valence force potential function containing all the interaction terms. These are given below :

1) PCl_3

For A_1 type vibrations

$$G \rightarrow \begin{vmatrix} 2{\cdot}898 \times 10^{22} & -1.456 \times 10^{30} \\ & 2.416 \times 10^{38} \end{vmatrix} \qquad F \rightarrow \begin{vmatrix} 2.67 \times 10^5 & 3{\cdot}15 \times 10^{-3} \\ & 5.384 \times 10^{-11} \end{vmatrix}$$

For E type vibrations.

$$G \rightarrow \begin{vmatrix} 4.01 \times 10^{22} & 1.403 \times 10^{30} \\ & 1.7995 \times 10^{38} \end{vmatrix} \qquad F \rightarrow \begin{vmatrix} 1.83 \times 10^5 & -4.696 \times 10^{-5} \\ & 1{\cdot}24 \times 10^{-11} \end{vmatrix}$$

2) $AsCl_3$

For A_1 type vibrations.

$G\rightarrow$ 2.14×10^{22} -5.145×10^{29} $F\rightarrow$ 2.39×10^{5} 2.57×10^{-3}
                        1.1154×10^{38} 4.32×10^{-11}

For E type vibrations.

$G\rightarrow$ 2.682×10^{22} 5.729×10^{29} $F\rightarrow$ 1.82×10^{5} -1.021×10^{-4}
                        1.1669×10^{38} 8.511×10^{-12}

3) $SbCl_3$

For A_1 type vibrations.

$G\rightarrow$ 2.0209×10^{22} -3.302×10^{29} $F\rightarrow$ 2.07×10^{5} 1.949×10^{-3}
                        8.34×10^{37} 3.2×10^{-11}

For E type vibrations.

$G\rightarrow$ 2.2773×10^{22} 2.961×10^{29} $F\rightarrow$ 1.59×10^{5} -3.48×10^{-5}
                        8.444×10^{37} 7.947×10^{-12}

Symmetry coordinates were used to derive the above matrices. Making use of proper transformation matrices the root mean square amplitudes of the bond distances during the totally symmetric stretching vibrations at a temperature of 300° K were obtained and the values are given in the following Table together with the interatomic distances.

Molecule	Bond distance in A units	Root mean square amplitude in A units
PCl_3	2	0.075
$AsCl_3$	2.16	0.0718
$SbCl_3$	2.325	0.0709

It has to be mentioned that the values of the root mean square amplitudes obtained here may depend on the actual potential energy function used apart from the slight error introduced because of the approximate expansion of the coth function. In order to avoid large discrepancies, a potential energy function containing all interaction terms is used in the calculations.

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Letters to the Editor

9

REFINED MOLECULAR STRUCTURE OF NAPHTHAZARIN

P. SRIVASTAVA

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32.

Approximate structure of naphthazarin $C_{10}H_4O_2(OH)_2$, form II, (Borgen, 1956), belonging to the space group, $P2_{1/c}$, has already been determined at room temperature by Srivastava (1958, 1960) and by Billy (1958). The present communication deals with the refinement of its molecular structure by employing the low temperature Weissenberg technique and difference synthesis and least square method.

A single crystal of naphthazarin was subjected to a low temperature of -140°C and the Weissenberg photographs along a- and b-axis were taken in a semicylindrical camera of diameter 5.75 cm. The unit cell parameters at $-140°$C and $+30°$C (room temperature) are given below :-

	at $-140°$C	at $+30°$C
a	7.70±0.01 Å	7.90±0.01 Å
b	7.27±0.01 Å	7.27±0.01 Å
c	16.52±0.02 Å	16.91±0.02 Å
β	123°30′±5′	124°38′±5′

The b-axis has been found to remain unchanged in this temperature range.

The final atomic co-ordinates of the asymmetric unit are given in Table I. The electron-density projection on the plane (010) has been shown in Fig. 1. The difference map clearly indicates the position of hydrogen atoms in the molecule. Isotropic form of temperature parameter was used for individual atoms and the discrepancy factor R was found to be 0.11 (without including the hydrogen atoms). In case of the unobserved planes, half the minimum observed value of the structure factor was taken in the calculation of R.
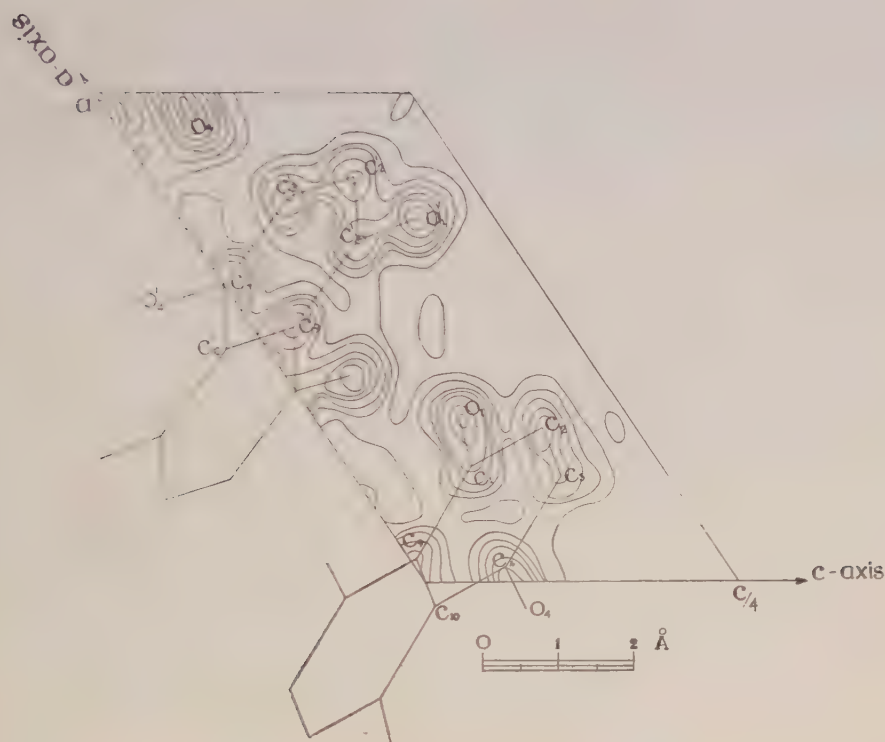
Fig. 1. Electron density projection along [010].

TABLE I

Atomic co-ordinates at −140°C.

	Molecule at 0,0,0				Molecule at a/2,0,0		
	X Å	Y Å	Z Å		X Å	Y Å	Z Å
C_1	1.8250	0.9000	1.6250	C'_1	5.3875	−0.5000	2.1500
C_2	2.4250	−0.0250	2.8875	C'_2	6.3750	0.6500	2.6500
C_3	1.6750	−1.2625	2.7250	C'_3	6.0750	1.7375	1.6375
C_4	0.2250	−1.5375	1.1750	C'_4	4.6875	1.6875	0.0000
C_9	0.3750	0.6250	0.0875	C'_9	4.0125	−0.5375	0.5250
O_1	2.5750	2.0250	1.9000	O'_1	5.7250	−1.4625	3.1250
O_4	−0.4250	−2.6875	1.0750	O'_4	4.4500	2.7000	−0.8750

The refined structure of naphthazarin is being published in detail elsewhere.

The author is thankful to Prof B. N. Srivastava, D.Sc., F.N.I., for his keen interest throughout the progress of this work   He also expresses his   sincere thanks to Dr. B. V. R. Murty, D.Phil and Dr. S. K. Dutta, Ph.D., for their valuable criticisms and suggestions and to Mr. A. S. Trivedi, M.Sc.. for his help in calculations.   The award of the C.S.I.R. Research Fellowship is also gratefully acknowledged.

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ON THE OPTICAL ABSORPTION SPECTRA OF $Ni^{2+}.6H_2O$ COMPLEX IN CRYSTALS

A. S. CHAKRAVARTY and R. CHATTERJEE

DEPARTMENT OF MAGNETISM,

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,

JADAVPUR, CALCUTTA-32.

In crystalline electric field of symmetry O_h, the ^3F groundstate of the Ni^{2+} ion is split into three components $^3A_2$, $^3F_2$, $^3F_{1a}$ with successively increasing energy. In considering the absorption spectra, the transitions to the upper ^3P level as also the forbidden transition to the singlets ^1D, ^1G and ^1S with low transition probabilities should be taken into account. All these transitions have energies of the order of 10^4 cm^{-1} and since they take place only in combination with suitable vibrational transitions, the intensities of the light absorptions must be lower than if they had been due to pure electronic transitions. The three main transitions $^3A_2 \rightarrow {}^3F_2$, $^3A_2 \rightarrow {}^3F_{1a}$ and $^3A_2 \rightarrow {}^3F_{1b}$ (^3P) give rise tob road bands called hereafter I, II and III over which the other weaker lines are superimposed.

For the aqueous solutions of several hydrated salts of Ni^{2+}, Dreisch *et al.* (1937, 1939) found that the peak of band I lies at 8300 cm^{-1}, peak of band II at 14100 cm^{-1} and peak of band III at 25000 cm^{-1}. This has been confirmed by Hartmann and Muller's (1958) observation of the absorption spectra of $NiSO_4$, $6H_2O$ and $NiSO_4$, $7H_2O$ crystals. Hartmann and Muller (1958; cf. Mookherjee *et al.* 1960) have been able to resolve the bands II and III into several peaks, e.g., band II into three peaks C, D, E of more or less the same intensity and a of much smaller intensity; band III into two peaks F, G of nearly the same intensity as the peaks of II, and three other b, c and d of much smaller intensity. They obtained further two more very weak peaks e, f near 39000 cm^{-1}. They could *apparently* explain all these peaks *except E*, on the basis of the splitting of the different states of the Ni^{2+} ion caused by a small tetragonal field superimposed upon cubic field (Fig. 1.).

Since the intensity of this band E is almost equal to the transitions from other Stark levels, it cannot be due to any intercombination between terms of different multiplicity (Orgel 1955). Contention of Ballhausen (1955) and Hartmann and Muller (1958) that the occurrence of this band is due to (L.S.) coupling effect has been also contradicted by Jorgensen (1958). On the other hand Mookherjee

et al (1960) have shown that the observed anisotropy of Ni^{2+} ion : $K_{\perp} - K_{11} = 354 \times 10^{-6}$, assuming a tetragonal field, does not agree with the splitting $C \rightarrow D \approx 300$
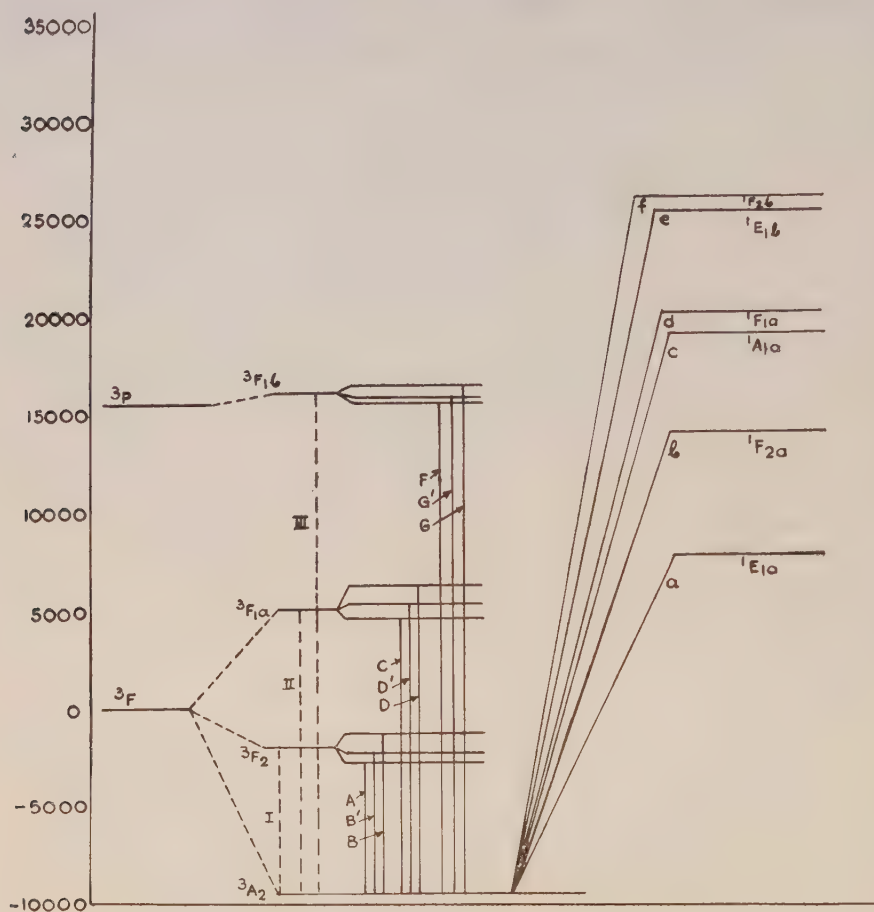
Energy level diagram of Ni(H$_2$O)$_6{}^{2+}$ ion under cubic
and orthorhombic field.
(Not drawn to scale)

cm^{-1} but with the splitting $C \rightarrow E \approx 1300$ cm^{-1}. In that case the peak D remains unexplained. Paramagnetic resonance studies of several salts of Ni^{2+} by Griffiths and Owen (1952) show that the electric field in all these salts has really an orthorhombic symmetry. We have therefore assumed an orthorhombic field in all these salts and been able to prove that all the three peaks C, D and E are really due to transitions from ground $3A_2$ level to the three components of the level $^3F_{1a}$ split up by the orthorhombic field.

We have neglected the effect of the spin-orbit interaction, which being a second order effect, is not so important in the case of optical absorption of Ni^{2+},

$6H_2O$ complex and the inclusion of this in the Hamiltonian would unnecessarily complicate the present calculations, meant to explain the existing experimental facts, as far as they go.

Following the method of Van Vleck (1932), and Schlapp and Penney (1932), Tanabe and Sugano (1954), Pryce and Runciman (1958) and taking into consideration all the energy states as already mentioned, we have calculated the energy levels of Ni^{2+}, $6H_2O$ with the following cubic and orthorhombic field parameters (Table 1), and compared them with the experimental values obtained by the aforementioned authors. All things considered the fit is much better than that obtained by Hartmann and Muller. Authors have also worked out a complete theory of the susceptibility of Ni^{2+} ion in an orthorhombic field which will be discussed in a future communication.

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TABLE I

Cubic field parameter $D_q = 810$ cm^{-1}
Orthorhombic field parameters $\qquad \sigma = -70$ cm^{-1}, $\qquad \delta = 20$ cm^{-1}
Racah parameters $\quad B = 1030$ cm^{-1} $\quad C = 4850$ cm^{-1}

Splittings	Calculated values $\times 10^{-3}$ cm^{-1}.	Experimental values $\times 10^{-3}$cm^{-1}.
$^3A_2\,(^3F) \rightarrow ^3F_2(^3F)$	7.957 (A)	
	8.010 (B') I	8.300
	8.097 (B)	
$\rightarrow ^3F_{1a}(^3F)$	14.130 (C)	13.900
	14.405 (D) II	14.200
	15.423 (E)	15.200
$\rightarrow ^1E_{1a}(^1D^1G)$	17.230 (a)	17.500
$\rightarrow ^1F_{2a}\,(^1D^1G)$	24.811 (b)	23.900
$\rightarrow ^3F_{1b}\,(^3P)$	25.030 (F)	
	25.080 (G') III	25.400
	25.120 (G)	
$\rightarrow ^1A_{1a}\,(^1D^1G)$	26.941 (c)	26.900
$\rightarrow ^1F_1\,(^1D^1G)$	30.160 (d)	30.050
$\rightarrow ^1E_{1b}\,(^1D^1G)$	35.879 (e)	
$\rightarrow ^1F_{2b}\,(^1D^1G)$	36.399 (f)	39.000
$\rightarrow ^1A_{1b}\,(^1S)$	67.929 (g)	—

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